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PROCEEDINGS

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AMERICAN ACADEMY

OF

ARTS AND SCIENCES.

VOL. XXX.

PAPERS READ BEFORE THE ACADEMY.

AID IN THE WORK DESCRIBED IN THIS PAPER WAS GIVEN BY THE ACADEMY FROM THE C. M. WARREN FUND FOR CHEMICAL RESEARCH.

I.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE CASE SCHOOL OF APPLIED SCIENCE.

XIX. — ON THE DETERMINATION OF SULPHUR IN VOLATILE ORGANIC COMPOUNDS.*

BY CHARLES F. MABERY.

Presented April 11, 1894.

THE great quantity of products introduced into the petroleum industry from the fields in Ohio and Canada yielding the sulphur oils has involved many sulphur determinations, and the necessity of a rapid method capable of affording results of extreme accuracy, especially in oils containing a small fraction of one per cent of sulphur. Several of the older methods leave nothing to be desired in point of accuracy, but they are not sufficiently expeditious for service in manufacturing operations, or in investigations which depend upon immediate information concerning the percentage of sulphur.

The first attempt to determine sulphur in organic compounds by combustion in oxygen was made by C. M. Warren,† the sulphuric acid formed being absorbed within the combustion tube in plumbic peroxide.

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* This paper is one of the series on the composition of the sulphur petroleums.

† These Proceedings, VI. 472.

The oxides and acids formed by combustion were first distilled and collected in bromine water as an oxidizing agent by Sauer [*] and this method was still further improved by Mixter, [†] who avoided the use of a rubber cork in the forward end of the combustion tube, carried forward the volatilized substance by a current of carbonic dioxide, and suggested more efficient means for oxidation by bromine and absorption. All these methods depend upon the formation of sulphuric acid and precipitation as baric sulphate, which involves considerable labor when a large number of determinations are necessary in a limited time. To overcome this difficulty Burton [‡] suggested a modification of the method of Sauer, which consists in absorbing the oxidized sulphur in a standard solution of potassic hydrate and titrating the excess of alkali with standard sulphuric acid.

Besidès these methods the only other suitable means for the determination of sulphur in oils with large percentages of sulphur is the well known method of Carius, in which the substance is oxidized in a closed tube by means of fuming nitric acid. In its applicability to all classes of compounds, and in the accuracy of results of which it is capable, this method leaves little to be desired except perhaps in the analysis of oils containing less than one hundredth of one per cent of sulphur. On account of the limited weight of substance that can be oxidized in a Carius tube another method must be selected for substances containing less sulphur. Our experience has shown that the Carius method may be relied upon in sulphur determinations to yield concordant results within a few hundredths of one per cent. Oxidation of the less volatile oils containing a small percentage of sulphur, without doubt, may be accurately accomplished in an open vessel, but with larger amounts of sulphur the action of nitric acid is so violent that it must entail loss by volatilization, unless indeed the sulphur oil is considerably diluted by a sulphur-free oil, in which case the solvent must be completely oxidized.

The great number of sulphur determinations in crude oils and products obtained from them, connected with the extended examinations which have occupied my attention during several years past, has demanded a careful comparison of the various methods as to their efficiency and economy of time. Particular attention has been given to details of the Carius method, with the precautions necessary in its successful application to the analysis of sulphur oils. The first requisite is a furnace of suitable construction to maintain an equal temperature, easily controlled in all the tubes within the furnace, without a great loss of heat by radiation. For this purpose and for Carius analyses in general I have recently had a furnace constructed which differs in certain features from any other I have seen, and it shows such a high degree of efficiency that a brief description may not be entirely devoid of interest. The body is of the ordinary cylindrical form, 75 cm. long and 25 cm. in diameter, of heavy sheet iron, and it is surrounded by two outer jackets of sheet iron each enclosing a half-inch space, and extending beneath on either side to within 6 cm. of the heating tube; it is supported upon legs of strap iron three sixteenths of an inch thick and two inches wide, each entirely encircling the body at either end for rigidity. These two air spaces retain the heat so effectually that the hand may be borne on the outside of the furnace when the thermometer within indicates a temperature of 200°. The iron tubes are as usual of gas pipe, with threads at either end with caps easily movable by the fingers. With a small hole in each cap for the escape of gas, these tubes retain all glass in the most violent explosions. When several tubes are in the furnace at the same time a record of them may conveniently be kept by suspending metal tags numbered consecutively from the holes in the caps by means of bent wire.

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[*] Fres. Zeit. Anal. Chem., XII. 32.

[†] Amer. Chem. Journ., II. 396.

[‡] Ibid., XI. 72.

Figure 1 shows the arrangement of the outer air spaces with the position of the heating tube. The furnace is heated by means of a gas stove heater 45 cm. in length, with thirty-two gas jets that will burn continuously with a flame 2 mm. high, giving a temperature within the furnace of less than 60°; by interposing an asbestos or an iron plate a considerably lower temperature may be maintained. The heating tube is supported on two iron straps bolted to the legs, one at either end of the furnace; by means of it the heat is very equally distributed with little waste, and the glass tubes being thus evenly heated there is less danger of loss by explosion. A temperature of 200° may be obtained within twenty-five minutes after lighting the jets, and it may be maintained with jets fifteen millimeters in height, requiring a small consumption of gas; the hand may be held without discomfort for some time directly beneath the heater. The variation in temperature at different heights within the furnace is small; with the thermometer at 275° at the level of the upper tubes, the tempera-

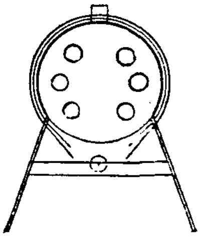
FIG. 1.

ture at the level of the lower tubes is about 9° higher. For temperatures higher than 275° a second heating tube is necessary.

It is frequently convenient to be able to regulate within close limits the flow of gas for the required temperature without further attention after lighting the jets. The device shown in Figure 2, which suggested itself for this purpose, consists in attaching to the end of the gas valve by means of a screw thread a brass cap with an index of stout copper wire moving in front of a graduated circle with a radius of about six inches.

With glass tubes of large size, — those we use are 1.5 mm. inside diameter, — well sealed and with strict adherence to certain conditions which have elsewhere been described by A. W. Smith and me,* there is little danger of an explosion. The quantity of nitric acid should not be in excess of twenty times the weight of the substance taken, and after heating to 175° for fifteen hours the tubes are opened, — best without removing from the furnace, — resealed and heated again to 250° during five to ten hours. The serious objection to the Carius method for sulphur is the slow process of oxidation, and it seems hardly possible to hasten the operation by raising the temperature, since glass tubes will not stand the great pressure.

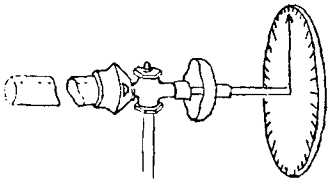

FIG. 2.

In studying various methods depending upon the oxidation of sulphur by combustion I have found that nothing less than complete oxidation gives reliable results. Many experiments on fractional combustion have shown clearly that compounds with high percentages of sulphur do not yield concordant results, even when the sulphur compound is diluted with a sulphur-free oil. I have found Burton's adaptation of the Sauer method reliable and expeditious, and with certain modifications presently to be described it is perfectly satisfactory for the analysis of oils of high as well as low percentages of sulphur. In Figure 3 the inlet tube for oxygen or air is shown as entering through the rear stopper, as proposed by Mixter, and extending just to the centre of the constriction. In the combustion of some of the oils which we have under examination, the temperature must be maintained as high as the most infusible Bohemian glass will stand, and at such temperatures the smaller tube within is distorted if it is placed in the forward portion of the combustion tube in the zone of greatest heat; if it terminates at the narrowest point of the constriction, continuous combustion is insured by thorough admixture of the volatilized substance with oxygen. Complete oxidation is still more certain in rapid combustion if that portion of the tube in front of the narrower part is left somewhat longer than is preferred by Sauer, Mixter, or Burton. The tubing we have in use is somewhat thicker in the wall than that in ordinary use, and larger, with an inside diameter of 18 mm. It is important that the oxidation proceed as rapidly as is consistent with complete absorption, and we find that this is best accomplished in a large U tube partly filled with broken glass. Our U tube is 34 cm. in height, 25 mm. inside diameter, and with 50 c. c. of the absorbent solution a rapid gaseous stream may be passed through without danger of loss. For low sulphur oils we use a solution of sodic hydrate of such a strength that 1 c. c. equals 0.0010 gram of sulphur, and for higher percentages a solution in which 1 c. c. equals 0.0050 gram. Methyl orange has been used as an indicator in all our determinations; the change in color in titrating an alkaline solution with this indicator is well defined and exceedingly delicate. The titrations may be made in the U tube without transferring the solution after washing in the acid from the combustion tube. To carry forward the volatilized substance it is advantageous to introduce a slow current of carbonic dioxide, as proposed by Mixter, and we have sometimes used a combustion tube closed with a rubber cork in front and sometimes a bent tube. With substances containing a high percentage of sulphur it is doubtless safer, as Mixter suggests, to avoid the use of a cork in front.

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* Amer. Chem. Journ., XVI. 83

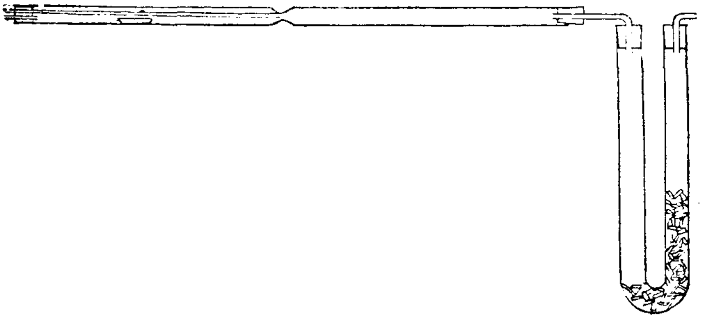

FIG. 3.

On account of the large consumption of oxygen in burning rapidly a considerable weight of oil, — at least three times the quantity theoretically required for oxidation, — and finding that the combustion proceeds with equal facility in air, nearly all our determinations have been made in a current of air supplied under pressure, with the same means for exhaustion that Burton found advantageous. The operation requires close attention and 0.5 to 1 gram of oil may easily be burned in forty-five minutes to one hour, depending upon the nature of the substance, the heavier oils especially if containing much sulphur being the most difficult to burn. The higher sulphides will not support a continuous flame, and dependence must be placed upon a very hot tube; with the more volatile oils it is sometimes difficult to maintain a continuous flame even in oxygen, the combustion proceeding in long intermittent non-luminous flashes. If the flame becomes luminous the rapidity of volatilization must be instantly checked, and the flow of air increased. The appearance of white fumes in the forward part of the combustion tube or the absorption tube, indicating improper adjustment as to the temperature, flow of gas, or rate of volatilization, is invariably attended with low results. The completeness of the absorption in the U tube was tested by placing a second tube beyond it containing a similar solution, but no trace of acid was found in the second tube when the excess of alkaline hydrate in the first at the end of the analysis was not less than 15–20 c. c. With a smaller excess in rapid combustions there is danger of loss. The oil for analysis is weighed in a bulb or tube of hard glass, and it is sometimes convenient to transfer most of it to a platinum or a porcelain boat, which may easily be accomplished without loss within the combustion tube provided there is a gentle current of air inward and the combustion tube in front has previously been heated to the required temperature.

In the examination of Ohio and Canadian sulphur petroleums for identification of the paraffine, aromatic, and unsaturated hydrocarbons, sulphur compounds, and other constituents, with which I am at present engaged, numerous determinations of sulphur have been necessary, and the extreme convenience of combustion in air has greatly facilitated the separation of the various products. As an evidence of the reliability of this method, the following results are selected with parallel determinations by the Carius method: —

	Percentage of Sulphur.	
	Combustion in Air.	Carius.
Distillate from crude Canada oil collected at 89°–91° after one distillation under 50 mm. and seven under atmospheric pressure	0.044	0.043
Distillate from crude Ohio oil collected at 127°–129° after one distillation under 50 mm. and seven under atmospheric pressure	0.0343	0.036
Distillate from crude Canada oil collected at 115°–117° after one distillation under 50 mm. and seven under atmospheric pressure	0.173	0.0108
Distillate from crude Canada oil collected at 120°–130° after one distillation under 50 mm. and five under atmospheric pressure	0.505	
The same after shaking five times with alcoholic mercuric chloride	0.07	
The same after shaking once with alcoholic mercuric chloride with the addition of solid mercuric chloride	0.086	
	I. II.	
Sulphur oil from Canada sludge acid	6.3 6.3	6.47
Sulphur oil from Canada sludge acid	17.36	17.31
	I. II.	
Sulphur oil from Canada sludge acid	16.67 16.76	
Canada sulphur oil	6.15	6.01
Canada sulphur oil	13.67	13.70
Crude sulphide separated by mercuric chloride from fraction 110°–115° of sulphur oil after the fifth distillation under 50 mm.	18.85	
A fraction of the same corresponding to pentyl sulphide, percentage of sulphur, 18.39		I. 18.53 II. 18.55 III. 18.67

These results were obtained by six persons working independently of one another.

The oxidation of nitrogen to any considerable extent by the use of air in the combustion of sulphur compounds is evidently excluded by the close agreement of the results it yields with corresponding determinations by the Carius method. In accordance with the suggestion of a friend, from the fact that nitrous and nitric acids are formed to a greater or less extent depending upon conditions in the ordinary forms of combustion, it seemed of interest to ascertain whether these acids were present at all in the alkaline absorbent. In testing for the formation of nitrous acid, the exceedingly delicate color reaction was applied which is produced in an acid solution of a nitrite by the addition of sulphanilic acid and naphthylamine chloride. An examination of our reagents showed that the purest commercial sodic or potassic hydrate gives an intense color, and even hydrates prepared from the metals are not free from color. Pure sulphuric acid gave no reaction, and pure sodic carbonate only a faint color. We finally obtained a solution that gave not a trace of color by dissolving metallic sodium and boiling the solution for some time with metallic aluminum. With this solution as the absorbent in a combustion of a sulphur oil, after the analysis the solution was as free from color as before when it had stood half an hour after the addition of the reagents. Since a pink color is distinctly visible in this reaction with one part of nitrogen in the form of nitrous acid in one thousand million parts of solution, it is safe to conclude that nitrous acid is not one of the products in this form of combustion.

To determine whether nitric acid is formed, after the combustion a portion of the sodic hydrate solution was neutralized, mixed with ferrous sulphate, and concentrated sulphuric acid poured beneath the solution. No color was visible at the junction of the two liquids. In a second test another portion of the alkaline solution was nearly neutralized with sulphuric acid, evaporated to dryness, and a few drops of phenolsulphuric acid added. Upon diluting to a definite volume, no difference could be perceived between the color of this solution and that given by phenolsulphuric acid alone in a blank experiment. In the combustion of sulphur oils in air, therefore, the atmospheric nitrogen is not affected.

For efficient aid in studying the details of these methods of analysis, I should acknowledge my obligations to Mr. W. O. Quayle, and to my assistants, Messrs D. B. Cleveland and G. M. Little.

II.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE, UNDER THE DIRECTION OF PROFESSOR JOSIAH P. COOKE.

DOUBLE HALOID SALTS OF ANTIMONY, CALCIUM, AND MAGNESIUM, WITH OBSERVATIONS ON THE REMARKABLE DISSOCIATION OF THESE COMPOUNDS.

By Francis Gano Benedict, A. M.

Presented by J. P. Cooke, May 9, 1894.

In a recent paper,* we described the results of our study of the double haloids of antimony and the alkaline metals. Since then we have extended the investigation to the corrresponding compounds with calcium and magnesium, and, although the work is still in an unfinished state, it must necessarily be interrupted for the present; and we therefore give here the results thus far obtained, the most important of which is *the complete dissociation of a definite crystalline salt at the ordinary temperature of the air.*

In the paper referred to,† a salt was mentioned having the composition $SbCl_3 . 2 KCl . 2 H_2O$, and the difficulties encountered in its preparation, analysis, and crystallographic study were discussed. Chief among these difficulties was the circumstance that the water of crystallization was lost wholly or in part at temperatures above —5° Cent., requiring the salt to be handled in a room below that temperature. In dealing with these new compounds the necessity for cold weather is even greater than in the case just mentioned. Hence the advancing of the season has prevented further work on this line. The research will be continued at the earliest opportunity.

Poggiale,‡ in 1845, was the first investigator to obtain double haloids of antimony and the earthy alkaline metals: "Le chlorure de barium, uni au chlorure d'antimoine, présente une particularité qui mérite d'être mentionée. Si la solution de chlorure de barium n'est pas concentrée les deux sels séparent par le refroidissement; le chlorure de barium cristallise en tables, tandis que le protochlorure d'antimoine décompose l'eau. Il faut donc pour obtenir cette combinaison, concentrer la solution de chlorure de barium, avant d'y ajouter le protochlorure d'antimoine. La liqueur donne alors des aiguilles fines disposées en groupes étoilés. Ce sel double est composé de

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* These Proceedings, XXIX. 212.

† *Loc. cit.*

‡ Comptes Rendus, XX. 1180.

$$SbCl_3 . 2\ BaCl + 5\ HO.$$

Le protochlorure d'antimoine se combine également avec les chlorures de strontium, de calcium et de magnesium."

Schäffer,[*] in 1860, working on the double iodides of antimony and the alkaline metals, described the double iodide of antimony and barium as a yellow salt with a formula,

$$2\ Ba\ I . SbI_3 + 18\ HO.$$

Storer [†] gives a list of salts, viz.: —

$2\ BaCl : SbCl_3 + 5\ Aq.$
$2\ CaCl : SbCl_3 + 5\ Aq.$
$2\ MgCl : SbCl_3 + 5\ Aq.$
$2\ SrCl : SbCl_3 + 5\ Aq.$

Watts's Dictionary [‡] gives the formula alone of a salt of this class, i. e. $2\ (BaCl_2 . SbCl_3)\ 3\ H_2O$.

Graham-Otto [§] makes the simple statement that antimonious chloride forms crystalline compounds with the chlorides of the alkaline and earthy alkaline metals.

Poggiale and Schäffer, therefore, appear to be the only investigators who succeeded in obtaining compounds with the earthy alkaline metals.

Although we have obtained a great many beautifully crystalline compounds from various mixtures of the haloids of antimony with the haloids of calcium, magnesium, barium, and strontium, only three of these have as yet been investigated. As has been before stated, cold weather is an absolute essential in the formation of the compounds, and the season is so far advanced that no more work can be done on them this year.

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[*] Pogg. Ann., CIX. 611.

[†] Dictionary of Solubilities, p. 149.

[‡] Edition of 1888, Vol. I. p. 287.

[§] Michaelis edition, Vol. II. p. 555.

The following salts have been prepared and analyzed, and the formulæ deduced for them are: —

I. $SbCl_3 . CaCl_2 . 8 H_2O$.
II. $SbBr_3 . CaBr_2 . 8 H_2O$.
III. $SbBr_3 . MgBr_2 . 8 H_2O$.

The materials used in the preparation of these salts were obtained as follows. The antimonious chloride and calcic chloride were the "chemically pure" products of the market. The antimonious bromide was made by the direct union of finely powdered metallic antimony and bromine in carbon bisulphide, after the manner described by Professor Cooke.* The calcic bromide and magnesic bromide were made by the action of pure hydrobromic acid upon pure calcic carbonate and magnesic carbonate respectively.

No difficulty was experienced in obtaining the three salts just named by mixing their components in approximately molecular proportions, adding just enough free acid to effect the complete solution of the antimony salt and evaporating the mixture in a crystallizing dish in a vacuum over sulphuric acid. Fortunately there was a room in the laboratory in which the temperature could be regulated quite easily so as to keep it at about 0° Cent. and not let it fall low enough to solidify the mixtures, thus offering the most favorable conditions to crystallization. The large isolated crystals were removed in the cold room, crushed in a mortar, hastily rubbed between filter papers and placed in glass-stoppered weighing bottles. Of necessity this operation required considerable dexterity to prevent any change in weight, but experience has shown that the whole operation can be performed in 45 to 50 seconds, with no appreciable change in the composition of the salt.

With but one exception the analysis of these salts presented no great difficulty.

Antimony was determined in the usual manner, by weighing as antimonious sulphide. All the precautions of this determination, as advised by Professor Cooke in his fundamental work on the atomic weight of antimony,† were closely observed.

Bromine and chlorine were determined as their respective silver salts. The presence of tartaric acid necessary for the solution of the antimony salt interferes to some extent in this determination by pre-

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* These Proceedings, XIII. 52.
† Ibid., XIII. 1–114.

cipitating that crystalline salt "silver emetic," discovered by Wallquist[*] and further studied by Professor Cooke.[†]

However, if care is taken to have only a slight excess of silver nitrate over the calculated amount, and to precipitate from dilute solutions, the probable error is reduced to a minimum.

Calcium was determined by igniting calcic oxalate precipitated in the usual way, and weighing as calcic oxide. This method was very satisfactory. Magnesium was weighed as magnesic pyrophosphate ($Mg_2P_2O_7$) formed by the ignition of the ammonic magnesic phosphate (NH_4MgPO_4) precipitated in the usual manner.

The presence of tartaric acid evidently interferes to some extent with the perfect working of this determination; but as the per cent of magnesium in the salt was so small the error was not prominent.

The determination of the water of crystallization presented the first serious difficulty, for, drying the salt in an air bath at 98°–100° showed rapid decomposition. In fact, no temperature was found at which the water would all go off and the salt remain undecomposed.

On placing the salt in a vacuum desiccator the loss was considerably greater than theory would require, till finally the residue amounted to but about 24% of the whole amount of salt used. Even in an ordinary desiccator there was a gradual loss in weight, and constancy was only reached when the residue was about 24% of the total mass, as before. At the suggestion of Professor Cooke the salt was intimately mixed with a quantity of ignited oxide of magnesia (heavy) in a crucible and heated to constant weight. In this operation it was necessary to get the upper layer of magnesic oxide hot before heating the lower part of the crucible containing the compound. Should any antimony haloid be volatilized, it would be decomposed upon reaching the hot layer of oxide of magnesium. This method served excellently for the first salt, i. e. $SbCl_3 . CaCl_2 . 8\,H_2O$. The oxide of magnesia seemed to retain the antimonious chloride readily, but when the same process was applied to the analysis of the bromides it was found that the magnesic oxide would not retain all of the bromide of antimony. The escape of this salt was clearly observed by the color of the flame held over the mouth of the crucible.

After several trials, a modification of the apparatus described by Jannasch and Locke[‡] was decided upon as giving the most satisfactory results. For this purpose some litharge was heated to constant weight, thereby expelling all the carbonic acid gas and moisture. The weighed salt from a weighing bottle was mixed with several grams of the ignited lead oxide in a porcelain boat large enough to fit a combustion tube of two centimeters internal diameter. This was placed in a kerosene oven and dry air drawn through it. Upon heating, the water expelled was absorbed in two weighed U tubes containing sulphuric acid and phosphoric pentoxide respectively. The apparatus for drawing dry air through the combustion tube was devised, and described at length by Professor Cooke in his paper on "A New Method of Determining Gas Densities." *

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[*] Gmelin, Handbook, Cavendish ed., X. 326.

[†] These Proceedings, XVII. 5.

[‡] Zeitschrift für Anorgan. Chemie, VI. 174.

This process for determining water is an ideal one, every trace of the antimony haloid being retained, and the water passing off freely at a moderate temperature, 250°. The results were surprisingly constant.

Although these several analyses are not as concordant with theory as one would wish, yet, when the instability of the compound, the necessarily hasty drying of the salt (freeing from mother liquor), and the difficulties of purification, are taken into consideration, the results are not at all beyond a reasonable limit of error.

In all three cases we could deal with large isolated crystals. There was no case of a complex crystalline precipitate, for all three compounds are most perfectly crystalline, and the only sources of contamination are occlusions of mother liquor and imperfect drying due to the haste required in transferring the salt to the weighing bottle. All three salts are decomposed by water, and are soluble in tartaric, hydrochloric, and hydrobromic acids. The last two solvents must be somewhat concentrated, as an excess of water decomposes the antimony salt.

I. $SbCl_3 . CaCl_2 . 8 H_2O$.

This is a beautifully crystalline salt, individual crystals often occurring over one inch in length. They are large, colorless plates, apparently belonging to the triclinic system. Their tendency to effloresce and decompose prevented any very satisfactory crystallographic examination, although traces of biaxial structure were observed with a polariscope. The salt loses all the water of crystallization and all the antimonious chloride in a desiccator over sulphuric acid, leaving a residue of nearly anhydrous calcic chloride.

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* These Proceedings, XXIV. 213, and American Chem. Journal, XI. 521.

a. 0.3607 gram of salt gave 0.1259 gram of antimonious sulphide.
b. 0.4342 gram of salt gave 0.0526 gram of calcic oxide.
c. 0.2322 gram of salt gave 0.3499 gram of argentic oxide.
d. 1.0737 grams of salt gave 0.3154 gram of water.

	Calculated[*] for $SbCl_3 . CaCl_2 . 8 H_2O$.	Found.
Antimony	24.95	24.93
Calcium	8.31	8.65
Chlorine	36.82	37.26
Water	29.92	29.37
	100.00	100.21

II. $SbBr_3 . CaBr_2 . 8 H_2O$.

This salt crystallizes well in large tabular crystals, often exceeding half an inch in length. Aside from the fact that the polariscope showed no interference figure, no crystallographic study of the salt could be made owing to its unstable nature. This salt, precisely as its analogue above, loses all its water of crystallization and also the antimonious bromide in a desiccator, till finally a nearly anhydrous residue of calcic bromide is left. Analysis gave the following results: —

a. 0.3742 gram of salt gave 0.0896 gram of antimonious sulphide.
b. 1.1896 grams of salt gave 0.0909 gram of calcic oxide.
c. 0.3090 gram of salt gave 0.4191 gram of argentic bromide.
d. 0.8415 gram of salt gave 0.1720 gram of water.

	Calculated for $SbBr_3 . CaBr_2 . 8 H_2O$.	Found.
Antimony	17.07	17.10
Calcium	5.68	5.46
Bromine	56.79	[†]57.72
Water	20.47	20.44
	100.00	100.72

III. $SbBr_3 . MgBr_2 . 8 H_2O$.

This salt crystallizes very well in large well defined tabular crystals, apparently isomorphous with the preceding salt. Large well shaped crystals gave no interference figure with the polariscope. This salt, as the others, loses all its water of crystallization and antimonious bromide in a desiccator over sulphuric acid, leaving a residue of magnesic bromide. Analysis gave the following results: —

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[*] Atomic weights used: Sb = 120; Cl = 35.456; Ca = 40; H = 1.0075; O = 16; Br = 79.955; Mg = 24.36.

[†] This excess of 1% of Br is probably due to the fact that the substance was not perfectly freed from mother liquor rich in hydrobromic acid; approaching warm weather would not permit of purification by recrystallization.

a. 0.9131 gram of salt gave 0.2193 gram of antimonious sulphide.
b. 1.1178 grams of salt gave 0.2128 gram of magnesic pyrophosphate.
c. 0.5160 gram of salt gave 0.7044 gram of argentic bromide.
d. 0.7013 gram of salt gave 0.1469 gram of water.

	Calculated for $SbBr_3 \cdot MgBr_2 \cdot 8H_2O$.	Found.
Antimony	17.40	17.15
Magnesium	3.54	4.06
Bromine	58.07	58.09
Water	20.99	20.95
	100.00	100.25

These three salts possess two important relations: —

1. Entire uniformity of structure, i. e. one molecule of the alkaline haloid combining with one molecule of the antimony haloid, and the resulting compound crystallizing in each case with eight molecules of water.

2. Each salt completely dissociates at the ordinary temperatures in a desiccator.

The most striking feature of this research is the above mentioned phenomenon. On attempting to estimate the water of crystallization by desiccation, an irritating odor first indicated a decomposition which was conclusively proven by the continual loss in weight. When constancy in weight was obtained, the residue on treating with water gave a hissing sound, and dissolved to a perfectly clear solution. This solution, on acidifying with hydrochloric acid and adding a solution of hydrogen sulphide, gave no precipitate, indicating an absence of antimony.

In the case of the salt $SbCl_3 . CaCl_2 . 8 H_2O$, the per cent of residue was 24.64, while the theoretical per cent of calcic chloride in the salt is 23.04. The excess would naturally be attributed to water which the calcic chloride would not readily yield to the sulphuric acid in the desiccator. The strong smell (volatilized antimony haloid) in the desiccator was observed long before the theoretical amount of loss calculated as water, i. e. 29.92%, had taken place. This showed that the antimony haloid had escaped before all the water had left the mass.

In the case of the double bromides, a singularly beautiful phenomenon took place. The antimonious bromide would sublime and crystallize all over the edge of the powdered mass of salt in those characteristic fine colorless needles measured and described by Professor Cooke.* These crystals were for the most part of microscopic size, but some attained a length of two or three millimeters. On further desiccation they soon disappeared. As would be expected, a direct experiment showed that the salt $SbCl_3 . CaCl_2 . 8 H_2O$ decomposed much more rapidly than the salt $SbBr_3 . CaBr_2 . 8 H_2O$, under precisely similar conditions.

Richards,† in 1890, described a tetra ammon-cupriammonium bromide with a formula $CuBr_2 . 6 NH_3$, which loses four molecules of ammonia in a desiccator, forming $CuBr_2 . 2 NH_3$. Although the escape of ammonia from its compounds is not uncommon, yet we believe this is the nearest case to the one in point, inasmuch as the loss here is perfectly definite.

The escape of antimony haloids from these compounds at a low temperature has a very important bearing on the question of molecular combination. It is almost universally admitted that the relation of the water of crystallization to a salt is different from that of its other components. A study of these compounds, however, shows that there is apparently no greater affinity between the two haloids than between the compound and the water of crystallization. Hence, in whatever manner the latter is combined, it is reasonable to suppose a similar union of the two haloids. If, therefore, the crystal water of a salt is held in molecular combination, the evidence as set forth in this research would be interpreted as signifying a molecular union of the two haloids.

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* These Proceedings, XIII. 76.

† Berichte der deutsch. Chem. Gesell., XXIII. 3790.

III.

THE NORTH AMERICAN CEUTHOPHILI.

By Samuel H. Scudder.

Presented May 9, 1894

The Ceuthophili are wingless Locustarians in which the tarsi are distinctly compressed rather than depressed, with no pulvilli,* the hind tibiæ furnished on the outer margins above with spines of two distinct grades,† the fore femora without foramina or genicular spines, the hind femora with the angle of their insertion on the inner and not on the outer side beneath, and the antennæ strongly approximated at base. They are all apterous.

With the exception of the genus Troglophilus Krauss, with two species from European caverns, and the genus Talitropis Bol., with a single species from New Zealand, placed respectively at one and the other end of the series, they are known only from America; and with the further exception of Heteromallus Brunner, with two species from Chili, they are all peculiar to the United States and Northern Mexico. Here they include six genera and sixty-seven species, the genus Ceuthophilus alone containing above fifty species. The larger proportion of them, if not all (excepting *Udeopsylla nigra*), frequent dark places, such as burrows, pits, caverns, wells, hollow trees, and especially the crevices beneath fallen logs.

They were first made known in this country by the descriptions of Haldeman, Girard, and Harris, and before their time only a single species from this country had been described, by Burmeister. Not a species of the group, even the European, was known to Serville. My first systematic paper, in 1861, was a study of "Rhaphidophora" (Proc. Bost. Soc. Nat. Hist., VIII.) where seven of our species were described or catalogued; but their diversity was hardly fully recognized when in the following year I published my Materials for a Monograph of the North American Orthoptera (Bost. Journ. Nat. Hist., VII.), where eighteen species and five genera were characterized or indicated; since then a few more species have been described, by Thomas, Brunner, Bruner, Packard, Walker, Blatchley, and myself, until now the number of nominal species is twenty-eight, which must, however, be reduced by synonymy and by reference to other genera to twenty.

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* Brunner states that Gammarotettix has a single pulvillus on the first tarsal joint; but although the treading surface of this joint (as of the succeeding) is broad, I can find no indication of a true pulvillus.

† This feature is obscure in Gammarotettix, where there are alternating longer and shorter spines of such slight inequality as easily to be overlooked, and which in the Table of Genera given below is ignored.

In 1888, Brunner, in his Monographie der Stenopelmatiden und Gyllacriden (Verh. Zool.-bot. Gesellsch. Wien), subjected all the species known to him to systematic treatment; but as the larger part of our species and some of our genera were unknown to him, and the number of separately described species has multiplied so greatly while still not including, at least in Ceuthophilus, the half of our species, it has seemed desirable to undertake a revision of the group, so far as our native species are concerned, and in the genus Ceuthophilus to redescribe all the older forms, as well as to publish the novelties. Accordingly in the present paper thirty-eight additional species of the group are characterized, together with a new genus, while I shall further show the validity of Daihinia of Haldeman, which has been called in question by Brunner, and shall point out first that one of the genera thought to belong here should be separated as a member of a distinct group. The total number of genera from North America is therefore six, and of the species sixty-seven, while a number of other species are known to me imperfectly by a single sex or poor examples.

TROPIDISCHIA Scudder.

Tropidischia Scudd., Bost. Journ. Nat. Hist., vii. 440–441 (1862).

In his Monograph of the Stenopelmatidæ, Brunner von Wattenwyl, from the insufficient data given in my two statements regarding the structure of this creature, incorrectly surmised that this genus should be placed in the Ceuthophili, and was perhaps congeneric with Heteromallus, a Chilian genus. Since, however, the hind tibiæ are supplied above with spines of one grade only, it is plainly more nearly related to the Dolichopodæ, from which it may be distinguished by the similarly spined margins of the under surface. It seems to form a group apart, between the Dolichopodæ and Ceuthophili, and of equivalent value. It appears to come nearer Hadenœcus and Dolichopoda than to any other described genera.

In addition to the characters mentioned above and those given in previous descriptions, I may add that all the legs are tetraquetrous, with all the margins spined, the spines similar in character and uniformly crowded, excepting on the lower margins of the fore femora, the inner carina of which is sparsely spined, the outer carina unarmed; also the lower margins of the middle femora, both carinæ of which are sparsely spined on the apical half, and the hind femora, the four carinæ of which, even on the swollen portion, are armed excepting at the extreme base, though both the inferior carinæ are rather sparsely spined. There are no spines on the genicular lobes of the femora, excepting a very slight one on the posterior side of the middle femora. There are but two pair of calcaria on the hind tibiæ, the upper the longer and less than half as long as the first tarsal joint. The hind tarsi are very strongly compressed, carinate beneath without pulvilli, about two fifths as long as the hind tibiæ, the first joint nearly as long as the remaining joints together, the second and fourth joints of the same length and either of them three times as long as the third. Finally, the subgenital lamina of the male is ample, the hind margin entire, with minute styles, consisting of a single bluntly conical joint; and the ovipositor is slender, gently arcuate, tapering and acuminate, unarmed at tip.

TROPIDISCHIA XANTHOSTOMA.

Rhaphidophora xanthostoma Scudd.!, Proc. Bost. Soc. Nat. Hist., viii. 12 (1861).

Tropidischia xanthostoma Scudd.!, Bost. Journ. Nat. Hist., vii. 441 (1862).

Originally described from Crescent City, Cal. (A. Agassiz). I have since received both sexes from Mendocino, Cal., through the favor of Mr. J. Behrens.

TABLE OF THE GENERA OF CEUTHOPHILI.

a^1. Last palpal joint cleft apically on the under side. Descending lobes of the mesonotum but little longer than those of the pronotum; sides of fore and middle coxæ externally laminate, the lamination elevated to a denticle or compressed spine either mesially or (on middle legs) apically, occasionally (Hadenœcus) wanting on middle legs. Fore tibiæ not sulcate above; hind tibiæ with spines of two grades on both outer and inner margins of upper surface. Outer valves of ovipositor unarmed above before the apex.

b^1. Palpi long. Hind tibiæ usually considerably longer than the hind femora. Third hind tarsal joint only half or less than half as long as the second.

c^1. Vertex obscurely bituberculate at apex. Last palpal joint no longer or scarcely longer than the third, and cleft beneath only apically. Middle coxæ unarmed. Middle femora with a feeble genicular spine on posterior margin. Hind tibiæ with more than four pairs of spurs. First hind tarsal joint almost as long as the others together. Subgenital plate of male triangular and rather deeply and narrowly emarginate . . . . *Hadenœcus.*

c^2. Vertex not tuberculate. Last palpal joint distinctly longer than the third, cleft beneath for almost its entire length. Middle coxæ spined mesially. Middle femora with a distinct genicular spine on posterior margin. Hind tibiæ with only four pairs of spurs. First hind tarsal joint generally a third shorter than the rest combined. Subgenital plate of male ample and broadly emarginate . . . . *Ceuthophilus.*

b^2. Palpi short. Hind tibiæ shorter or at most but little longer than the hind femora. Third hind tarsal joint hardly shorter than the second, or (in Daihinia) wanting. (Lamination of middle coxæ produced inferiorly to the semblance of a spine.)

c^1. Third palpal joint as long as fifth, the inferior cleft of the latter extending over only the apical half. Middle femora unarmed at tip or with a very feeble spine. Hind tibiæ shorter or at least no longer than the hind femora, with few spines of the second grade on the upper surface, those of the first grade relatively numerous, at least in the ♀, more or less irregularly placed and of unequal length; the calcaria three in number on each side, the uppermost generally a little the longest and unusually distant from the extreme apex, so as to appear rather as an additional pair of spurs. Subgenital plate of male greatly produced and apically deeply fissured.

d^1. Descending lobes of mesonotum slightly longer than those of pronotum. Last tarsal joint very much shorter than the remaining joints together, the third joint normal, though but little shorter than the second. Subgenital plate of male ample, rather deeply and broadly emarginate, the sides extending backwards as slender threads . . . . *Phrixocnemis.*

d^2. Descending lobes of mesonotum no longer than those of pronotum. Last tarsal joint about as long as the rest together; third tarsal joint wanting (as also on fore legs). Subgenital plate of male immensely produced and so deeply fissured as to form two tapering ribbons . . . . *Daihinia.*

c^2. Third palpal joint shorter than the fifth, the inferior cleft of the latter extending its whole length. Middle femora with a genicular spine on posterior side. Hind tibiæ slightly longer than the hind femora, with numerous spines of the second grade uniform in length and pretty regularly separated; calcaria three in number on each side, the middle one much longer than the others. (First hind tarsal joint a third shorter than the rest combined.) Subgenital plate of male ample, apically bituberculate . . . . *Udeopsylla.*

a^2. (Vertex bituberculate. Palpi short), the last joint apically with no inferior cleft. Descending lobes of mesonotum considerably longer than those of pronotum; sides of fore and middle coxæ neither caridate nor spined. (Fore and middle femora unarmed.) Fore tibiæ sulcate above; hind tibiæ (of the same length as the hind femora) with only one grade * of spines above on the lateral margins; (calcaria two in number on each side, subequal and not long. Third hind tarsal joint half as long as the second. Subgenital plate of male ample, apically broadly and not deeply emarginate); outer valves of ovipositor serrate above before the apex . . . . . . *Gammarotettix.*

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* See introductory remarks.

HADENŒCUS Scudder.

Hadenœcus Scudd., Bost. Journ. Nat. Hist., vii. 439–440 (1862); Brunn., Monogr. Stenop., 66 (1888).

Table of the Species of Hadenœcus.

Body pale testaceous. Ovipositor nearly or quite as long as the body. Subgenital plate of ♂ broadly emarginate at apex. *cavernarum.*

Body dark brown. Ovipositor only half as long as the body. Subgenital plate of ♂ narrowly emarginate at apex . . *puteanus.*

Hadenœcus cavernarum.

Phalangopsis sp. Thomps., Ann. Mag. Nat. Hist., xiii. 113 (1844).

Rhapidophora cavernarum Sauss., Ann. Soc. Entom. France (4), i. 492 (1860).

Hadenœcus cavernarum Scudd.!, Proc. Bost. Soc. Nat. Hist., xii. 409 (1869); xix. 38 (1877); Boliv., Ann. Soc. Ent. France (5), x. 72 (1880); Riley, Stand. Nat. Hist., ii. 184, fig. 260 (1884); Comst., Intr. Ent., 114 (1888); Blatchl., Proc. Ind. Acad. Sc., 1892, 153.

Rhapidophora subterranea Scudd.!, Proc. Bost. Soc. Nat. Hist., viii. 8 (1861); Pack., Amer. Nat., v. 745, fig. 126 (1871); Cope, Ibid., vi. 409 (1872); Hubb., Amer. Ent., iii. 37 (1880).

Hadenœcus subterraneus Scudd.!, Bost. Journ. Nat. Hist., vii. 441 (1862); Walk., Catal. Derm. Salt. Brit. Mus., i. 201 (1869); Pack., Guide Ins., 565 (1869); Glover, Ill. N. A. Ent., Orth., pl. 8, fig. 6 (1872); Cope-Pack., Amer. Nat., xv. 882 (1881); Brunn., Monogr. Stenop., 66, fig. 34 (1888); Pack., Mem. Nat. Acad. Sc., iv. 67–70, 83, 116, fig. 16, pl. 17, fig. 3 (1888); Id., Psyche, v. 198–199 (1889); Garm., Ibid., vi. 105, fig. (1891).

Early notices of this insect by Telkampf will be found in Müller's Arch. Anat. Phys., 1844, 318, and Wiedemann's Arch. Naturg., 1844, 384; also by Schiödte in K. Danske Vid. Selsk. Skrift. 1849, 5; by Agassiz in Silliman's Amer. Journ. Sc., 1851, 127; and by Lesquereux in the Actes Soc. Helv. Sc. Nat., 40 Sess., 52–53 (1855).

I have studied specimens only from the Mammoth Cave, Ky. It is also reported by Packard from many other caves in the Mammoth Cave region, as Dixon's, White's, Salt, Ice, Diamond, Grand Avenue, Poynter's, Wetzel's, Haunted, and Emerson Spring Branch caves; besides Mail Robbers', One Hundred Dome, Walnut Hill Spring, Short, Proctor's, Little Lithographic, and Sugar Bowl caves, and a cave under Gardiner's Knob, — all near Glasgow Junction; also a cave near Baker's Furnace, and John and Fred's Cave on the east bank of Dismal Creek; further in Carter County caves, viz. Gray Tom's, Zwingle's, Bat, Van Meter's, Grayson Springs, and Burchell's caves; and finally in Nickajack Cave, Tenn. Blatchley also reports it from Wyandotte Cave, Ind., on the authority of Cope, but it is not so given by Cope in the references quoted; and Walker, of course in error, from the "west coast of America"! I have also seen specimens in the Museum of Comparative Zoölogy, Cambridge, from Turner's Caves, Pennington Gap, Lee County, Va. (H. G. Hubbard), and Ely Cave, Lee County, Va. (N. S. Shaler).

HADENŒCUS PUTEANUS.

Hadenœcus puteanus Scudd.!, Proc. Bost. Soc. Nat. Hist., xix. 37 (1877).

On sides and under covering of wells in North Carolina; also in Mississippi.

CEUTHOPHILUS SCUDDER.

Ceuthophilus Scudd., Bost. Journ. Nat. Hist., vii. 433–434 (1862); Brunn., Monogr. Stenop., 61 (1888).

This is one of the dominant American genera of Locustariæ, confined to North America and almost entirely to the United States, embracing a large number of species in every section of the country, of which fifty-five are here characterized. Several others are known to me by single specimens or mutilated examples. The following table is based principally upon the males. It has been impossible to construct it so as to bring together the allied species, whose relationship is better shown by the order in which they are described, though even here the arrangement is far from satisfactory, nearly allied species being sometimes separated at considerable distances in order to bring them in closer relation with other allies. Although I have had six hundred and fifty examples to study at this time, besides others in alcohol, the material is still insufficient to make a satisfactory disposition of our species, and I am confident that very many more yet remain to be discovered.

Table of the Species of Ceuthophilus.

a^1. Second joint of hind tarsi at least half as long again, usually twice or more than twice as long, as the third.

b^1. Fore femora one third or more than one third longer than the pronotum, at least in the ♂; hind tibiæ of ♂ almost always straight, never greatly bowed.

c^1. Hind tibiæ of ♂ at least a tenth longer than the hind femora.

d^1. Ovipositor much shorter than the fore femora.

e^1. Hind femora stout, not three times as long as broad, at least in the ♂ . . . . 1. *variegatus.*

e^2. Hind femora slender, four times as long as broad in the ♀ . . . . 2. *ensifer.*

d^2. Ovipositor much longer than the fore femora.

e^1. Hind tibial spurs less than twice as long as the tibial depth; outer carina of hind femora of ♂ generally with some spines at least half as long as the tibial spurs.

f^1. Fore femora of ♂ three fourths as long again as the pronotum . . . . 3. *stygius.*

f^2. Fore femora of ♂ from one half to two thirds as long again as the pronotum.

g^1. Hind femora of ♂ much less than four times as long as broad; hind tibiæ of ♂ very long and more or less sinuous at base in old individuals.

h^1. Largest spines of outer carina of hind femora of ♂ simple and similar to the others. 4. *gracilipes.*

h^2. Largest spines as above greatly tumid at base. 5. *latebricola.*

g^2. Hind femora of ♂ much more than four times as long as broad; hind tibiæ of ♂ scarcely more than one tenth longer than the hind femora, straight. 6. *grandis.*

e^2. Hind tibial spurs fully twice, generally much more than twice, as long as tibial depth; outer carina of hind femora of ♂ with no spines a third as long as the tibial spurs.

f^1. Armature of outer carina of hind femora of ♂ developed as distinct spines rather than as serrations; ovipositor arcuate . . . . 7. *secretus.*

f^2. Armature of outer carina of hind femora of ♂ developed only as recumbent serrations; ovipositor almost or quite straight.

g^1. Hind femora of ♂ slender, almost or quite four times as long as broad; hind tibiæ exceptionally long, nearly or quite one sixth longer than the femora.

h^1. Hind femora of ♂ more than twice as long as the fore femora; ovipositor very feebly arcuate, only two thirds as long as the hind femora.
8. *palmeri.*

h^2. Hind femora of ♂ less than twice as long as the fore femora; ovipositor straight, three fourths as long as the hind femora . . . 9. *corticicola.*

g^2. Hind femora of ♂ less slender, being less than three and three quarters times as long as broad; hind tibiæ but little more than one tenth longer than the femora . . . . 10. *varicator.*

c^2. Hind tibiæ of ♂ distinctly less than a tenth longer than the hind femora; ovipositor always longer than the fore femora.

d^1. Hind tibiæ of ♂ straight; outer carina of hind femora of ♂ never conspicuously spined.

e^1. Hind tibial spurs nearly three times as long as the tibial depth . . . . 11. *latibuli.*

e^2. Hind tibial spurs at most less than twice as long as the tibial depth, rarely half as long again.

f^1. Prevailing colors blackish fuscous above, the lighter colors being distinctly less extensive than the dark (which is generally nearly black) and appearing as dots or roundish spots, and sometimes also as a broad mediodorsal stripe.

g^1. Fore femora of ♂ at most scarcely more than a third longer than the pronotum; outer carina of hind femora of ♂ serrulate, not spined.

h^1. Hind femora relatively long and slender, three and three quarters times as long as broad.
12. *seclusus.*

h^2. Hind femora relatively stout, not over three and a half times longer than broad.

i^1. Hind tibiæ but little longer than the femora, the spurs not longer than the tibial depth, the hind femora considerably more than twice as long as the fore femora.

j^1. Hind femora less than three times as long as broad . . . . 13. *terrestris*.

j^2. Hind femora three and a half times as long as broad . . . . 14. *celatus*.

i^2. Hind tibiæ considerably longer than the femora, the spurs half as long again as the tibial depth, the hind femora only about twice as long as the fore femora . . . . . 15. *brevipes*.

g^2. Fore femora of ♂ nearly one half longer than the pronotum; outer carina of hind femora of male spined, not serrulate. . . . . . 16. *lapidicola*.

f^2. The lighter colors which are more massive prevail above, the darker appearing principally as posterior bands to the segments and rarely darker than fusco-castaneous, rarely with a light mediodorsal line.

g^1. Outer carina of hind femora of ♂ armed with only a few raised points.

h^1. Hind femora slender, nearly three and a half times longer than broad . . . 17. *arizonensis*.

h^2. Hind femora stout, about two and a half times longer than broad . . . . . 18. *uniformis*.

d^2. Hind tibiæ of ♂ arcuate or sinuous; outer carina of hind femora of ♂ always conspicuously spined.

e^1. Hind femora very long, four times as long as broad, the fore femora fully three fourths as long again as the pronotum . . . . 19. *heros*.

e^2. Hind femora relatively short, not more than three and a half times longer than broad, the fore femora considerably less than half as long again as the pronotum.

f^1. Inferior sulcus of hind femora of ♂ broadening proximally . . . . 20. *uhleri*.

f^2. Inferior sulcus of hind femora of ♂ of uniform width . . . . 21. *blatchleyi*.

b^2. Fore femora but little if any longer than the pronotum even in the male; hind tibiæ of male usually straight, but often bowed or sinuate.

c^1. Dorsal surface of abdomen of ♂ smooth and even.

d^1. Hind tibiæ of ♂ arcuate or sinuate in basal half.

e^1. Hind tibiæ of ♂ considerably longer than the femora; hind tibial spurs usually at least half as long again as the tibial depth.

f^1. Hind femora of ♂ relatively long, three and a half times as long as broad; no large spines on outer carina. 30. *maculatus.*

f^2. Hind femora of ♂ relatively stout, rarely exceeding three, never three and a quarter, times as long as broad; some spines on outer carina as long as the tibial spurs.

g^1. Hind tibiæ of ♂ at least a tenth longer than the femora.

h^1. Hind femora of ♂ two and a half times longer than the fore femora; hind tibial spurs only slightly longer than the tibial depth. 28. *meridionalis.*

h^2. Hind femora of ♂ but little more than twice as long as the fore femora; hind tibial spurs nearly twice as long as the tibial depth . 45. *inquinatus.*

g^2. Hind tibiæ of ♂ less than one tenth longer than the femora . . . . 22. *spinosus.*

e^2. Hind tibiæ of ♂ at most scarcely longer than the femora; hind tibial spurs rarely longer than the tibial depth.

f^1. Hind femora of ♂ three or more than three times as long as broad; fore femora nearly or quite a fifth longer than the pronotum.

g^1. Hind tibiæ of ♂ at most feebly sinuate at base. 39. *agassizii.*

g^2. Hind tibiæ of ♂ very strongly bowed. 34. *valgus.*

f^2. Hind femora of ♂ less than three times as long as broad; fore femora only an eighth longer than the pronotum.

g^1. Hind tibiæ of ♂ strongly bowed, armed below with a row of spines mounted on nodules. 33. *nodulosus.*

g^2. Hind tibiæ of ♂ faintly sinuate at base, normally armed beneath . . . . 51. *latipes.*

d^2. Hind tibiæ of ♂ straight throughout.

e^1. Outer carina of hind femora of ♂ armed with prominent conical spines, generally well separated.

f^1. Hind tibiæ of ♂ less than one tenth longer than the femora.

g^1. Dorsal surface of body almost uniformly very dark, almost black, the lighter markings themselves not very light nor extensive, and therefore inconspicuous.

h^1. Hind tibial spurs generally excessively divergent, extending in nearly opposite directions on the two sides and set at a high angle with the tibia. 35. *divergens.*

h^2. Hind tibial spurs rarely exceeding 120° in divergence, and set at an angle with the tibia not exceeding 50°.

i^1. Smaller species, with pallid sides, luteous legs, and narrow dorsal stripe, the hind tibiæ of the ♂ a twelfth as long again as the femora. 23. *cæcus.*

i^2. Larger species, with castaneous sides and legs and broad dorsal stripe, the hind tibiæ of ♂ not a thirtieth longer than the femora . 26. *sallei.*

g^2. Dorsal surface of body with conspicuously contrasted dark and light markings, neither prevailing over the other . . . . 47. *pallidus.*

f^2. Hind tibiæ of ♂ a tenth longer than the femora. 32. *bicolor.*

e^2. Outer carina of hind femora of ♂ more or less delicately serrate or armed with recumbent spines.

f^1. Body of male very compact, short subfusiform, not or hardly more than two and a quarter times as long as broad.

g^1. Hind femora of ♂ relatively stout, considerably less than three times as long as broad, the hind tibiæ longer than the femora, and the spurs only as long as the tibial depth . . . . 24. *nigricans.*

g^2. Hind femora of ♂ relatively slender, three times as long as broad, the hind tibiæ shorter than the femora and the spurs nearly half as long again as the tibial depth . . . . 25. *fusiformis.*

f^2. Body of ♂ much more elongated, rarely distinctly fusiform, over three and generally at least four times as long as broad.

g^1. Hind tibiæ of ♂ at least a tenth longer than the femora.

h^1. Body without conspicuously contrasted colors; hind femora of ♂ relatively slender, four times as long as broad . . . . 36. *occultus.*

h^2. Body with conspicuously contrasted colors; hind femora of ♂ relatively slender, less than three and a quarter times as long as broad . 46. *discolor.*

g^2. Hind tibiæ of ♂ less than one tenth longer than the femora.

h^1. Hind femora of ♂ with no raised points on the upper distal half.

i^1. Outer carina of hind femora of ♂ almost unarmed; markings of the body more or less marmorate or maculate.

j^1. A broad continuous light dorsal stripe on pronotum, usually extending over the whole thorax.

k^1. Hind tibial spurs distinctly marked with black at base; ovipositor twice as long as fore femora . . . . 27. *latens.*

k^2. Hind tibial spurs at most indistinctly infuscated at base; ovipositor shorter than fore femora . . . . . . 31. *tenebrarum.*

j^2. A narrow and very unequal light dorsal stripe on pronotum, interrupted, if present, on rest of thorax . . . . 38. *bruneri.*

i^2. Outer carina of hind femora of ♂ finely and closely serrate; dark markings of body confined to transverse borderings of the segments. 48. *vinculatus.*

h^2. Hind femora of ♂ with a greater or less number of raised points on upper distal half.

i^1. Hind femora of ♂ with only a few distant recumbent spines on outer carina.

j^1. Hind tibiæ of ♂ a tenth longer than the femora; spurs fully twice as long as tibial depth . . . . 44. *pinguis.*

j^2. Hind tibiæ of ♂ less than a tenth longer than the femora; spurs much less than twice as long as tibial depth . . 40. *mexicanus.*

i^2. Hind femora of ♂ with numerous denticulations on the outer carina, forming a more or less close serration.

j^1. Ovipositor relatively short, at most but little more than half as long as hind femora.

k^1. Hind femora of ♂ less than twice as long as fore femora.

l^1. Hind tibiæ of ♂ no longer than femora; spurs only a little longer than tibial depth, and divaricating about 60°; inner carina of fore femora minutely serratulate . . . . 50. *californianus.*

l^2. Hind tibiæ of ♂ a little longer than femora; spurs fully twice as long as tibial depth, and divaricating about 90°; inner carina of fore femora simply spined. 49. *testaceus.*

k^2. Hind femora of ♂ two and a fourth times as long as fore femora . . 29. *neglectus.*

j^2. Ovipositor relatively long, two thirds as long as hind femora or more.

k^1. Hind femora of ♂ relatively slender, at least three times as long as broad.

l^1. Hind tibiæ of ♂ of same length as femora; colors moderately dark. 37. *alpinus.*

l^2. Hind tibiæ of ♂ considerably longer than femora; colors rather pallid. 41. *pallescens.*

k^2. Hind femora of ♂ relatively stout, hardly more than two and a half times as long as broad . . . . . . 43. *crassus.*

c^2. Dorsal surface of abdomen of ♂ closely tuberculate; hind tibiæ strongly arcuate.

d^1. Both outer and inner carinæ of hind femora of ♂ armed with a large compressed spine as long as the depth of the genicular lobes . . . . 52. *pacificus.*

d^2. Outer carina of hind femora of ♂ elevated to a high lamina, suddenly terminating acutely before the genicular lobes . . . . 53. *henshawi.*

a^2. Second joint of hind tarsi but little longer than the third.

b^1. Large species; outer carina of hind femora considerably and uniformly elevated throughout . . . . 54. *devius.*

b^2. Small species; outer carina of hind femora elevated distally much more than proximally . . . . . . 55. *neomexicanus.*

The male being unknown to me, *C. sylvestris* does not appear in the above table. It will be found below as No. 41.

1. Ceuthophilus variegatus, sp. nov.

Blackish fuscous with a slight olivaceous tinge, marked with yellowish luteous; there is an interrupted dorsal stripe of the lighter color especially interrupted on the anterior half of the pronotum; this is heavily margined by subconfluent dark blotches or spots, and the dark color prevails over the rest of the thorax, with oblique patches of the lighter tints on the meso- and metanotum, irregular vermiculate blotches of greater or less extent on the pronotum and the lower edges of the descending lobes of the thorax margined not very narrowly with luteous; the sides of the abdomen are prevailingly luteous, but the anterior outer margins are mostly fuscous; the hind femora have the usual scalariform markings very pronounced, while the other legs are prevailingly luteous and much streaked with fuliginous, excepting the tarsi; the longer spines are bright luteous, but black tipped. The antennæ are two or three times as long as the body, moderately stout at the base and gradually tapering, and the legs moderately short. Fore femora distinctly broader than the middle femora, nearly half as long again (♂) or scarcely a fourth as long again (♀) as the pronotum, and less than half as long as the hind femora, the inner carina with three long spines, the distal subapical and very long. Middle femora with 2–3 long spines on the front carina, one subapical and very long, and on the hind carina 1–2 long spines besides a long genicular spine. Hind femora slightly (♂) or considerably (♀) more than twice as long as the fore femora, very broad and stout, distinctly less than three times as long as broad especially in the male, a few very distant and scattered raised points over the whole apical half of the surface, excepting beneath and especially on the inner side above, the outer carina with 3–4 very unequal spines in the apical half, one, sometimes two, much larger than the rest, coarse and as long as the tibial spurs (♂) or with a single inconspicuous spine in the pregenicular sinus (♀), the inner carina with half a dozen small uniform but irregularly distant spinules, the intervening sulcus rather narrow. Hind tibiæ straight in both sexes, moderately slender, scarcely expanded distally, distinctly but not greatly longer than the femora, armed beneath with a single subapical spine besides the apical pair; spurs subalternate, the basal before the end of the proximal fourth of the tibia, half as long again as the tibial depth. set at an angle of 40–45° with the tibia and divaricating about 50–60°, their tips considerably incurved; inner middle calcaria a little larger than the outer, twice as long as the others or as the spurs, and nearly as long as the first tarsal joint. Hind tarsi considerably less than half as long as the tibia, the first joint unusually prolonged below and as long as the rest together, the second fully twice as long as the third and with it as long as the fourth. Cerci moderately stout, regularly tapering, as long as the pronotum. Ovipositor very short, not so long as the pronotum, rapidly tapering at base, beyond slender, the armature of the inner valves consisting of moderately stout but rather prominent bluntly pointed spines.

Length of body, ♂ 15 mm., ♀ 19 mm.; antennæ (est.), ♂ 30+ mm., ♀ 45+ mm.; pronotum, ♂ 5.5 mm., ♀ 6.5 mm.; fore femora, ♂ 8 mm., ♀ 7.75 mm.; hind femora, ♂ 16.75 mm., ♀ 17.75 mm.; hind tibiæ, ♂ 19 mm., ♀ 18.5 mm.; ovipositor, 6 mm.

2 ♂, 2 ♀. Matamoras, Tamaulipas, Mexico, L. B. Couch; Ringgold Barracks at the lower end of the Rio Grande, C. A. Schott; Carrigo Springs, Texas, A. Wadgymar, through L. Bruner.

2. CEUTHOPHILUS ENSIFER.

Ceuthophilus ensifer Pack.!, Amer. Nat., xv. 882, pl. 7, figs. 4, 4ab (1881); Id.!, Mem. Nat. Acad. Sc., iv. 71-72, 83, figs. 17, 17ab (1888); Blatchl., Proc. Ind. Acad. Sc., 1892, 153 (1894).

Body luteo-testaceous, heavily marked with blackish fuscous, which broadly borders all the abdominal segments posteriorly and inferiorly, as it does also (but more or less broken mediodorsally) the thoracic; there are also two large subdorsal anterior blackish fuscous spots on the meso- and metanotum, and the pronotum has a large T-shaped blackish median spot heavily mapped out with a basal expansion and which is cut by a mediodorsal luteous line, bordered on either side posteriorly by one, anteriorly by two luteous dots, transversely aligned; the inferior border is broadly margined with black, leaving in the middle of either side a large irregular luteous blotch more or less streaked with fuscous; the legs are castaneous, the hind femora with fuscous scalariform markings and apically broadly annulate with fuscous; the apical half of tibiæ and the tarsi pallid. The antennæ are about twice the length of the body and the legs long and slender. The fore femora are not stouter than the middle femora, nearly twice as long as the pronotum and somewhat more than half as long as the hind femora, the inner carina with 3-4 spines of considerable size. Middle femora with four spines on the front carina and on the hind carina three besides a moderately long genicular spine. Hind femora about as long as the body, somewhat less than twice as long as the fore femora, slender, the apical third subequal, the inferior margin nearly straight, the whole fully four times as long as broad, the dark portions of the surface, even of the inner side, with slight, equally distributed raised points but none independent of them, the outer carina (♀) with delicate distant spinules especially beyond the middle, the inner carina similarly armed, the intervening sulcus moderately narrow. Hind tibiæ considerably longer than the femora, slender, armed beneath with a single preapical spine besides the apical pair; spurs rudely opposite, the basal well beyond the end of the proximal third of the tibia, half as long again as the tibial depth, set at an angle of 35° with the tibia and divaricating 90–100°, their tips strongly incurved; inner middle calcaria considerably longer than the outer, much more than twice as long as the others or as the spurs, but much shorter than the first tarsal joint. Hind tarsi almost half as long as the tibiæ, the first joint as long as the rest together, the second almost three times as long as the third and with it longer than the fourth. Cerci tapering throughout, finely pointed, half as long again as the femoral breadth. Ovipositor hardly three quarters as long as the fore femora, stout in basal third, tapering in middle third, slender and subequal in distal third, the apex produced and slightly upturned, the inner valves with eight sharp but slight serrations.

Length of body, ♀ 19.5 mm.; pronotum, 5.2 mm.; fore femora, 10 mm.; hind femora, 18.75 mm.; hind tibiæ, 20.25 mm.; ovipositor, 7 mm.

2 ♀. Nickajack Cave, Tenn.

3. CEUTHOPHILUS STYGIUS.

Rhaphidophora stygia Scudd.!, Proc. Bost. Soc. Nat. Hist., viii. 9 (1861); Pack., Amer. Nat., v. 745 (1871).

Ceuthophilus stygius Scudd.!, Bost. Journ. Nat. Hist., vii. 438 (1862); Walk., Cat. Derm. Salt. Brit. Mus., i. 202 (1869); Pack., Guide Ins., 565 (1869); Riley, Stand. Nat. Hist., ii. 184 (1884); Pack., Mem. Nat. Acad. Sc., iv. 70–71, 83 (1888); Brunn., Monogr. Stenop., 65 (1888); Blatchl., Proc. Ind. Acad. Sc., 1892, 148–149 (1894).

Ceuthophilus sloanii Pack.!, Ann. Rep. Peab. Acad. Sc., v. 93–94 (1873); Id.!, Mem. Nat. Acad. Sc., iv. 71, 83 (1888). Immature.

Body pale brown, the segments bordered posteriorly with dark brown or black, becoming gradually paler toward the hinder part of the body and dotted with pale spots; the markings in general closely resemble those of *C. gracilipes*, but the dark colors do not generally prevail to so great an extent as in that species. The antennæ, moderately coarse at the base, taper very gradually, and are of immense length, being more than four times the length of the body. The legs are very long and slender. Fore femora scarcely broader than middle femora, very slender, three fourths as long again as the pronotum, yet only about half as long as the hind femora, the inner carina armed with 2–5 spines. Middle femora with 2–5 spines on the front carina and on the hinder 1–3 spines besides a not very long genicular spine. Hind femora about as long as the body and twice the length of the fore femora, not very stout, about four times as long as broad, tapering gracefully, the apical third being subequal, the darker portions covered with exceedingly fine and subdued raised points, the outer carina with more or less slight distant serrations or triangular denticulations occasionally developing as spines, especially on the apical half, the inner carina with a few slighter distant similar serrations closest in the middle half, the intervening sulcus not very broad. Hind tibiæ slender, straight in both sexes, fully a tenth longer than the femora, armed beneath with 2–3 subapical spines besides the apical pair; spurs vaguely opposite or subopposite, the basal within the proximal fourth of the tibia, about half as long again as the tibial depth, set at an angle of about 40° with the tibia and divaricating about 90°, their tips much incurved; inner middle calcaria much longer than the outer, more than twice as long as the others or as the spurs and as long as the first joint of the tarsus, beset with short hairs, as are also the upper calcaria. Hind tarsi fully two fifths the length of the tibia, the first joint shorter than the rest combined, the second twice as long as the third and with it shorter than the fourth. Cerci rather long and slender, tapering to a fine point, fully half as long as the hind femora. Ovipositor three fifths the length of the hind femora, not greatly swollen at base, tapering gently in basal half, equal beyond and not very narrow, the tip scarcely upturned and not produced, the apex being nearly rectangular, the teeth of the inner valves feebly crenate.

Length of body, ♂ 17 mm., ♀ 19.5 mm.; pronotum, ♂ 5.5 mm., ♀ 5.3 mm.; fore femora, ♂ ♀ 9.75 mm.; hind femora, ♂ 19.5 mm., ♀ 20.1 mm.; hind tibiæ, ♂ 21.5 mm., ♀ 22.8 mm.; ovipositor, 13 mm.

1 ♂, 3 ♀. Hickman's Cave, Ky., A. Hyatt; cave in Crawford Co., Ind., W. P. Hay, through W. S. Blatchley. In the Museum of Comparative Zoölogy there are specimens taken at White's Cave, near Mammoth Cave, Ky.; Fountain's Cave, A. S. Packard; and One Hundred Dome Cave, near Glasgow Junction, Ky., F. G. Sanborn,

H. Garman. Packard, in his Memoir on Cave Animals, reports it also from Little and Great Wyandotte Caves, a cave in Washington Co., and Georgetown, Floyd Co., all in Indiana, and also from the following caves in Kentucky: Diamond Cave, near Mammoth Cave, John and Fred Field Cave, near Dismal Creek, Bee Spring and Laurel Caves, Carter Co. According to Brunner, specimens seen by him come from Texas. *C. slounii* was described from caves in Kentucky and Bradford, Ind.

4. CEUTHOPHILUS GRACILIPES.

Phalangopsis gracilipes Hald., Proc. Amer. Assoc. Adv. Sc., ii. 346 (1850); Walk., Cat. Derm. Salt. Brit. Mus., i. 116 (1869).

Rhaphidophora gracilipes Scudd. !, Proc. Bost. Soc. Nat. Hist., viii. 7 (1861).

Ceuthophilus gracilipes Scudd. !, Bost. Journ. Nat. Hist., vii. 439 (1862); Walk., Cat. Derm. Salt. Brit. Mus., i. 202 (1869); Scudd. !, Rep. U. S. Geol. Surv. Nebr., 249 (1872); Brunn., Monogr. Stenop., 62–63 (1888); Smith, Cat. Ins. N. J., 409 (1890); McNeill. Psyche, vi. 27 (1891).

Ground color of body varying from luteous to dark castaneous, very heavily marked with blackish fuscous, so that the latter is often or perhaps generally the prevailing tint; the darker colors prevail always on the hinder half of all the segments but the pronotum and sometimes, especially in young specimens, to such an extent that all parts behind the pronotum are blackish fuscous, dotted with luteous; in the lightest colored specimens, the dark coloring prevails on the pronotum along the anterior and especially the posterior margins, and is generally present in a subdorsal posterior tongue emitted on either side from the anterior margin; the anterior edge of the dark posterior markings of each segment, especially in the front portion of the body, is exceedingly irregular and broken, and the lightest parts are more or less and irregularly clouded with fuscous; the femora are usually of the prevailing tint of the body, but, even when the body is dark, are sometimes luteous throughout as the tibiæ and tarsi always are, except for occasional infuscation of the former at base; the outer sides of the hind femora have the characteristic markings of the genus more or less distinct. Antennæ moderately coarse at base, tapering with great regularity, 3–4 times the length of the body. Legs very long and slender. Fore femora no stouter than the middle femora, more than half as long again as the pronotum, especially in the ♂, distinctly less than half as long as the fore femora, the inner carina usually with 2–3 spines, often rather long in old individuals, especially the distal ones. Middle femora with 3–4 spines on either carina, the hind carina with a not very long genicular spine. Hind femora as long as or longer than the body, considerably more than twice the length of the fore femora, very stout at base, but gradually diminishing in stoutness so that the distal third is slender and subequal and the whole less than three and a half times longer than broad, the surface mostly glabrous, but on the darker portions above beset not very sparsely with feeble raised points, the outer carina with about thirteen distant unequal rather coarse spines, the longest shorter than the tibial spurs (♂) or almost unarmed (♀), the inner carina much less elevated than the outer, with equal abortive denticulations numerous in the ♂, infrequent and equidistant in the ♀, the intervening sulcus moderately broad. Hind tibiæ rather slender, straight or in old male specimens gently subarcuate or slightly waved in the proximal third, nearly a sixth longer than the femora, armed beneath usually with two aligned preapical spines besides the apical pair; spurs subopposite, the basal pair near end of proximal fourth of tibia, less than half as long again as the tibial depth, set at an angle of about 40° with the tibia and usually divaricating about 60°, but sometimes to as much as twice that, incurved especially at tip; inner middle calcaria much longer than the outer, more than twice as long as the other calcaria, about twice the length of the spurs, but much shorter than the first tarsal joint. Hind tarsi much less than half as long as the tibia, the first not so long as the rest together, the second nearly three times as long as the third and with it fully as long as the fourth. Cerci stout at base, tapering throughout, nearly a third as long as the hind femora. Ovipositor with the basal third rather stout, beyond equal and rather slender, nearly three fourths the length of the hind femora, the armature of inner valves acicular, arcuate, elongate.

Length of body, ♂ 19 mm., ♀ 23 mm.; antennæ, ♂ (est.) 75 mm.; pronotum, ♂ 5.75 mm., ♀ 6.75 mm.; fore femora, ♂ 10 mm., ♀ 10.6 mm.; hind femora, ♂ 21.5 mm., ♀ 22 mm.; hind tibiæ, ♂ 24.75 mm., ♀ 25 mm.; ovipositor, 15.5 mm.

22 ♂, 11 ♀. Maryland, New Jersey, P. R. Uhler; Ithaca, N. Y., Comstock; Blockton, Florida (C. Caule, Jr.), J. H. Comstock; Southern Illinois, P. R. Uhler; Illinois, Walsh, Webster; Northern Illinois, R. Kennicott; Minnesota; Red River, Manitoba, D. Gunn; Nebraska City, Nebr., F. V. Hayden. It has also been reported from Pennsylvania by Haldeman, and from Georgia and Colorado by Brunner.

5. CEUTHOPHILUS LATEBRICOLA, sp. nov.

Blackish fuscous, sometimes almost piceous, glabrous, profusely spotted with luteous or rufo-luteous and more or less blotched with the same on the thoracic segments, though nowhere in large masses, but, except the luteous bordering of the inferior margins, more as if through the confluence of minute spots. There is always a narrow mediodorsal line or stripe on the thoracic segments with slight expansions anteriorly and posteriorly on the pronotum; legs luteous with heavy blackish infuscations at the femoral tips, the hind femora heavily marked with fuscous scalariform markings. The antennæ are slender and about three times as long as the body, and the legs moderately long and slender. Fore femora no stouter than the middle femora, considerably less than half as long as the hind femora, a little more (♂) or a little less (♀) than a third longer than the pronotum, the inner carina with a long preapical spine and sometimes another much smaller. Middle femora with 2–4 spines on the front carina and on the hind carina with 1–2 spines besides a long genicular spine. Hind femora about as long as the body, considerably more than twice as long as the fore femora, moderately stout, in the male somewhat strongly constricted before the genicular lobes, about three and a quarter times longer than broad (♂), the surface with only a few raised points along the upper edge interiorly, the outer carina considerably elevated before the constriction, armed with 6–9 unequal teeth, the largest tumid at base and not so long as the tibial spurs (♂) or with 2–3 feeble serrations (♀), the inner carina with distant feeble minute spinules (♀), the intervening sulcus slender. Hind tibiæ sinuate in the proximal half (♂) or straight throughout (♀), considerably longer than the femora (scarcely longer in Eastern examples), armed beneath with a single subapical spine besides the apical pair; spurs subopposite, the basal just before the end of the proximal third of the tibia, about half as long again as the tibial depth, set at an angle of 45° with the tibia and divaricating 100°, their apical third incurved; inner middle calcaria very much longer than the outer, almost twice as long as the others or as the spurs and nearly as long as the first joint of the tarsi. Hind tarsi not a third as long as the tibiæ, the first joint longer than the rest together, the second fully twice as long as the third and with it at least as long as the fourth. Cerci rather stout, rapidly tapering, a little longer than half the femoral width. Abdomen roundly truncate in the male. Ovipositor straight, two thirds as long as the hind femora, gently tapering in basal third, beyond equal and slender, the tip considerably upcurved and very acuminate, the teeth of the inner valves aculeate.

Length of body, ♂ 15 mm., ♀ 15.5 mm.; antennæ, ♂ 52 mm.; pronotum, ♂ 5 mm., ♀ 4.75 mm.; fore femora, ♂ 6.9 mm., ♀ 6 mm.; hind femora, ♂ 15.5 mm., ♀ 13.5 mm.; hind tibiæ, ♂ 17.5 mm., ♀ 14.5 mm.; ovipositor, 9 mm.

4 ♂, 6 ♀. Lexington and Tyrone, Ky. (S. Garman); Washington, D. C., Wright; Centre Co., Penn., Shaler; and Petroleum, Ritchie Co., W. Va. (Mus. Comp. Zoöl.).

6. CEUTHOPHILUS GRANDIS, sp. nov.

Body dark luteo-castaneous very heavily marked with blackish or blackish fuscous, which is heaviest at the posterior margins of all the segments, along the front margin of the pronotum, and in a stripe bordering the broad mediodorsal rufo-luteous stripe of the pronotum; the anterior lower angle of the pronotum, and to some extent that of the other thoracic segments, are dull luteous, merging with the luteous of the central portion of the descending lobes; on the abdomen the darker colors prevail above to such a degree that the luteous appears to be maculate on a dark ground; antennæ and legs luteo-testaceous, more or less though generally feebly infuscate, the hind femora with fuscous scalariform markings, apically broadly marked with fuscous but preceded by a broad more or less clearly marked luteous annulation. The antennæ are slender except near the base and fully four times as long as the body, the legs very long and slender. Fore femora scarcely stouter than the middle femora, barely half as long as the hind femora, two thirds (♂) or three fifths (♀) as long again as the pronotum, the inner carina with 3–4 spines none of them very long nor very unequal. Middle femora similarly armed on the front carina and on the hind carina 3–4 spines besides the moderately long genicular spine. Hind femora as long as the body, very little more than twice as long as the fore femora, pretty stout at base, but with the slender portion much produced, the apical third or in the female even more than that being subequal, the whole being in the male nearly four and a half times longer than broad, the surface above and on both sides just beyond the middle with a few scattered raised points, the outer carina armed throughout all but extreme base with 8–12 distant, not greatly unequal, subequidistant spines, the longest scarcely so long as the tibial spurs but tumid at base (♂) or with similarly distant feeble serrulations (♀), the inner carina sparsely (♂) or very sparsely (♀) serrulate, the intervening sulcus narrow. Hind tibiæ straight in both sexes, fully a tenth longer than the femora, armed beneath with 1–2 subapical spines (one sometimes paired) besides the apical pair; spurs subopposite, the basal at about the end of the proximal third of the tibia, slightly longer than the tibial depth, set at an angle of 50–60° with the tibia and divaricating about 120°, their tips much incurved; inner middle calcaria very much longer than the outer, fully twice as long as the others or as the spurs and nearly as long as the first joint of the tarsi. Hind tarsi two fifths as long as the tibiæ, the first joint about as long as the rest together, the second nearly three times as long as the third and with it as long as the fourth. Cerci slender and delicately tapering, a quarter as long again as the femoral breadth. Ovipositor more than half as long as the hind tibiæ, the lower margin straight, not stout and gently tapering in the basal half, slender and equal in the apical half, the tip upturned and bluntly acuminate, the teeth of the inner valves triangular and rather long, straight.

Length of body, ♂ 19 mm., ♀ 23.5 mm.; antennæ (est.), ♂ 90 mm.; pronotum, ♂ ♀ 6.7 mm.; fore femora, ♂ 11.25 mm., ♀ 10.75 mm.; hind femora, ♂ 22.8 mm., ♀ 23.4 mm.; hind tibiæ, ♂ 25 mm., ♀ 25.6 mm.; ovipositor, 13.5 mm.

1 ♂, 2 ♀. Chattanooga, Tenn., J. W. Martin (U. S. Nat. Mus.).

This species is not far removed from *C. gracilipes* in structural details, though with much duller and less diversified markings.

7. CEUTHOPHILUS SECRETUS, sp. nov.

In markings this species agrees altogether with *C. palmeri* except that the luteous colors are clearer and that the abdomen is more completely fuscous, the luteous being almost entirely confined to a narrow stripe across the anterior margin, not seen when the segments are contracted. The antennæ are fully three times the length of the body, slender and gradually tapering, the legs long and slender. Fore femora scarcely stouter than middle femora, considerably more than half as long again as the pronotum and about half as long as the hind femora, the inner carina with 1–3 small spines. Middle femora with 2–4 spines of varying length on the front carina, and on the hind carina occasionally a single small spine besides the long genicular spine. Hind femora nearly as long as the body, about twice the length of the fore femora, tapering with no abruptness, nearly four times as long as broad, the apical fourth subequal, with scattered but nowhere numerous minute raised points on the upper apical half, the outer carina with small but rather coarse unequal spines, mostly next the narrower portion of the femora, the longest less than a third as long as the tibial spurs, the inner carina with similar but smaller and subequal spines throughout its extent, on both far more delicate in the female than in the male, the intervening sulcus decidedly narrow. Hind tibiæ straight in both sexes, slender, about an eighth longer than the femora, armed beneath with two subapical spines besides the apical pair; spurs scarcely subopposite, the basal at the end of the proximal third of the tibia, almost or quite twice as long as the tibial depth, set at an angle ordinarily of 30–40°, but sometimes of more nearly 80° with the tibia, divaricating 100–160°, their tips incurved; inner middle calcaria considerably longer than the outer, nearly twice as long as the others or as the spurs, but much shorter than the first tarsal joint. Hind tarsi almost half as long as the tibiæ, the first joint as long as the rest together, the second three times as long as the third and with it longer than the fourth. Cerci slender, tapering, half as long again as the femoral breadth. Ovipositor fully three fourths as long as the hind femora, gently and uniformly arcuate throughout, of equal width throughout, the tip not sharply acuminate, the inner valves with a feebly crenulate armature.

Length of body, ♂, ♀ 17.5 mm.; pronotum, ♂ 4.6 mm., ♀ 4.9 mm.; fore femora, ♂ 8 mm., ♀ 7.8 mm.; hind femora, ♂ 16 mm., ♀ 14.75 mm.; hind tibiæ, ♂ 18 mm., ♀ 16.5 mm.; ovipositor, 11.6 mm.

6 ♂, 2 ♀. Dallas, Texas, Boll.

8. CEUTHOPHILUS PALMERI, sp. nov.

Dark fuscous heavily blotched and spotted with dull luteous, the lighter markings consisting of a broken mediodorsal stripe of generally varying and greater or less width, of very irregular blotches and tortuous streaks on the sides of the pronotum, of large anterior spots on the sides of the meso- and metanotum, and of anterior transverse dashes or belts on the abdominal segments; the fore and middle legs are fusco-luteous becoming more or less deeply fuscous at the distal extremity of the femora and proximal end of the tibiæ, the hind femora fuscous except at base with the usual dull luteous markings, the rest of the leg dull luteous, but the basal half of the tibiæ more or less infuscated. The antennæ are three or four times as long as the body, and very slender except toward the base, and the legs long and slender. Fore femora no stouter than the middle femora, about three fifths as long again as the pronotum and half or less than half as long as the hind femora, the inner carina with 2–4 mostly long spines. Middle femora with 1–2 spines besides a long subapical one on the front carina, and on the hind carina 2–3 spines besides a very long genicular spine. Hind femora nearly as long as the body, fully twice as long as the fore femora, stout basally but rapidly tapering so that the apical third or more is subequal, nearly four times as long as broad, with no raised points, both carinæ distantly and finely serrulate in the apical half, a little finer and more distant in the female than in the male, the intervening sulcus not very broad. Hind tibiæ straight in both sexes, fully a sixth longer than the femora, armed beneath usually with two subapical spines besides the apical pair; spurs subalternate, the basal a little beyond the proximal fourth of the tibia, nearly three times as long as the tibial depth, set at an angle of about 50° with the tibia and divaricating 110–130°, their tips considerably incurved; inner middle calcaria a good deal longer than the outer, fully twice as long as the others or as the spurs, but shorter than the first joint of the tarsi. Hind tarsi more than two fifths the length of the tibiæ, the first joint as long as the rest together, the second three times as long as the third and as long as the fourth. Cerci very long and slender, but shorter than the fore femora. Ovipositor two thirds as long as the hind femora, very feebly arcuate, rather slender, tapering gently throughout, a little upturned and very acutely pointed at tip, the apical teeth of the inner valves delicate and finely pointed, but not very long, especially the proximal.

Length of body, ♂ 23 mm., ♀ 19 mm.; pronotum, ♂ 6 mm.; ♀ 5.75 mm.; fore femora, ♂ 9.8 mm., ♀ 9 mm.; hind femora, ♂ 19.5 mm., ♀ 18 mm.; hind tibiæ, ♂ 23.5 mm., ♀ 21 mm.; ovipositor, 12 mm.

14 ♂, 14 ♀. From the darkest recesses of the side caverns of a bat cave 48 × 20 feet in size, of which the roof had fallen in, in Georgetown, Williamson Co., Texas, E. Palmer; New Braunfels, Texas, H. E. Scudder; Texas, Schaupp in coll. S. Henshaw. The New Braunfels specimen is referred to under *C. californianus* in Bost. Journ. Nat. Hist., vii. 438.

9. CEUTHOPHILUS CORTICICOLA, sp. nov.

Dark fuscous feebly marked, at least on the pronotum, with cloudy dull luteous vermiculations, especially on the lower part of the descending lobes, which are generally edged more distinctly with luteous; legs of the color of the body or lighter, the anterior pairs more or less infuscated near the femoro-tibial articulation, the distal part of the tibiæ and tarsi more clearly luteous; hind femora with the usual markings, growing luteous toward the base. The antennæ are slender and three or more times as long as the body, the legs long and slender. Fore femora faintly stouter than the middle femora, more than half as long again as the pronotum and fully half as long as the hind femora, the inner carina with 2–3 long spines. Middle femora with 2–3 pretty long spines on the inner carina, and on the outer two small ones besides a long genicular spine. Hind femora about as long as the body, nearly twice as long as the fore femora, moderately stout in the basal half, but the swollen portion short, the apical third being subequal and the whole about four times as long as broad, the upper half with a very few scattered raised points apically, the outer carina feebly delicately and distantly serratulate on the distal half, more delicately in the ♀ than in the ♂, the inner carina similarly but more closely spined throughout, the intervening sulcus narrow. Hind tibiæ straight in both sexes and slender, nearly a sixth longer than the femora, armed beneath with 1–2 subapical spines besides the apical pair; spurs subalternate, the basal just beyond the proximal fourth of the tibia, fully twice as long as the tibial depth, set at an angle of about 45° with the tibia and divaricating 100–120°, their tips incurved; inner middle calcaria distinctly longer than the outer, more than twice as long as the others or as the spurs, and nearly equal to the first tarsal joint. Hind tarsi nearly half as long as the tibiæ, the first joint as long as the rest together, the second three times as long as the third, and nearly equal to the fourth. Cerci very long and slender, beyond the inflated basal portion tapering very gradually, as long as the fore femora. Ovipositor long and straight, fully three quarters as long as the hind femora, the base rather slender and tapering, the distal half or more slender and equal, the extreme tip scarcely upturned but very acute, the inner valves with an armature of fine but not very long pointed teeth.

Length of body, ♂ 17.5 mm., ♀ 19.5 mm.; pronotum, ♂ 5.2 mm., ♀ 5.75 mm.; fore femora, ♂ 8.2 mm., ♀ 8.75 mm.; hind femora, ♂ 15.75 mm., ♀ 17 mm.; hind tibiæ, ♂ 18.4 mm., ♀ 18.75 mm.; ovipositor, 13 mm.

5 ♂, 2 ♀. Dallas, Texas, Boll. Texas, Belfrage, in woods under bark, and coming to the light at night in September.

10. CEUTHOPHILUS VARICATOR, sp. nov.

Dull testaceous, heavily infuscated especially on the thoracic segments which are more fuscous than testaceous, the latter appearing on the pronotum principally as an impure fuscous-streaked blotch in the middle of either lateral half, more or less connected posteriorly by a transverse bar; a transverse anterior series of four testaceous dots; on the other thoracic segments appearing in large anterior lateral spots more or less confluent; legs fusco-testaceous, becoming luteous apically, the hind femora testaceous with scalariform fuscous markings, the other femora darker apically than at base. The antennæ are tolerably stout at base but soon taper to a delicate thread and are about three times as long as the body, and the legs moderately long and slender. Fore femora no stouter than the middle femora, nearly half as long as the hind femora, and more than a third longer than the pronotum (♂ ♀), the inner carina armed with 2–3 spines, the subapical very long. Middle femora similarly armed on the front carina, and on the hind carina 1–2 moderate spines besides a very long genicular spine. Hind femora a little more than twice as long as the fore femora, moderately slender, being almost three and three quarters times as long as broad (♂), the apical fourth subequal, the surface with no raised points, the outer carina entirely unarmed except for 4–5 very distant slight recumbent serrations on the apical half, more distinct in the ♀ than in the ♂, the inner carina with a few raised points, the intervening sulcus narrow. Hind tibiæ straight in both sexes, slender, fully a tenth longer than the femora, armed beneath with two median subapical spines besides the apical pair; spurs subalternate, the basal at or beyond the end of the proximal fourth of the tibia, more than twice as long as the tibial depth, set at an angle of about 80° with the tibia and divaricating about 150°, their extreme tips incurved; inner middle calcaria very much longer than the outer, about twice as long as the others, or as the spurs, and just about as long as the first tarsal joint. Hind tarsi more than two fifths the length of the tibiæ, the first joint longer than the rest together, the second three times as long as the third, and as long as the fourth. Cerci slender, tapering, a third as long again as the femoral breadth. Ovipositor two thirds the length of the hind femora, faintly arcuate throughout, equal from close to the base, moderately broad, the tip scarcely upturned, acutangulate (about 40°), the inner valves feebly crenulate, the prominences slightly accentuated.

Length of body, ♂ 17 mm., ♀ 20 mm.; antennæ (est.), ♂ 50 mm., ♀ 58 mm.; pronotum, ♂ 5.25 mm., ♀ 6.4 mm.; fore femora, ♂ 7.5 mm., ♀ 8.9 mm.; hind femora, ♂ 15.75 mm., ♀ 18 mm.; hind tibiæ, ♂ 18 mm., ♀ 20 mm.; ovipositor, 12 mm.

1 ♂, 1 ♀. Waco, Texas, July 13 (Mus. Comp. Zoöl.). 3 ♀ from Columbus, Texas, are in the Riley collection (U. S. National Museum).

11. CEUTHOPHILUS LATIBULI.

Ceuthophilus latibuli Scudd.!, Ins. Life, vi. 313–314 (1894).

Dark brownish fuscous, heavily blotched with ferrugineo-testaceous, largely in the form of small longitudinally ovate spots more or less regularly disposed on the dorsum, but inclined to become confluent on the sides, and forming blotches on the pronotum, the hind femora dark with two series of longer and an intermediate series of shorter oblique testaceous lines, forming scalariform markings, all the tarsi and at least the distal half of the tibiæ pallid luteous. The antennæ are slender and fully three times as long as the body, and the legs long and slender. Fore femora slightly stouter at base than the middle femora, half as long again as the pronotum, considerably less than half as long as the hind femora, the inner carina armed with 2–4 longer or shorter spines on the distal half. Middle femora with two or three usually long spines besides a subapical long spine on the front carina, and on the hind carina a very long genicular spine, besides sometimes an additional spine. Hind femora about as long as the body, considerably more than twice as long as the fore femora, rather stout, but more than the distal fourth slender and subequal, the whole three (♂) to three and a half (♀) times as long as greatest breadth, the surface very finely and uniformly scabrous with delicate raised points on the darker portions, the outer carina slightly prominent, furnished with 8–9 rather unequal inequidistant short spines, the longest not half the length of the tibial spurs (♂) or unarmed (♀), the inner carina with 13–16 small inequidistant (♂) or 6–8 inconspicuous (♀) spines, the intervening sulcus rather deep but of moderate width. Hind tibiæ much longer than the femora, straight in both sexes, slightly compressed at the base, armed beneath with 1–2 median subapical spines, besides the apical pair; spurs not opposite, the basal generally at or before the end of the proximal fourth of the tibia, nearly or quite three times as long as the tibial depth, set at an angle of about 60° with the tibia and of about 120° more or less with each other, slightly incurved at tip; inner middle calcaria very slender, considerably longer than the outer, twice as long as the others or as the spurs and considerably longer than the first tarsal joint. Hind tarsi distinctly less than half as long as the tibiæ, the first joint not nearly so long as the rest combined, the second twice as long as the third and with it shorter than the fourth. Cerci slender, delicately tapering, about as long as the femoral breadth. Ovipositor straight, rather slender, from a third to more than one half as long as the hind tibiæ, the tip hardly upcurved and exceedingly acute, the denticulations of the inner valves triangular, hardly aculeate.

Length of body, ♂ 18 mm., ♀ 17 mm.; antennæ, ♂ 55+ mm., ♀ (est.) 65 mm.; pronotum, ♂ 5 mm., ♀ 6 mm.; fore femora, ♂ 8 mm., ♀ 8.5 mm.; hind femora, ♂ ♀ 18 mm.; hind tibiæ, ♂ ♀ 19.5 mm.; ovipositor, 10 mm.

7 ♂, 5 ♀. Crescent City, Fla., in burrows of the gopher (*Gopherus polyphemus*), H. G. Hubbard; Georgia, H. K. Morrison.

12. CEUTHOPHILUS SECLUSUS, sp. nov.

Glabrous, blackish fuscous, heavily and irregularly marked with luteous becoming rufo-luteous dorsally, the whole surface about equally divided between the fuscous and luteous, but the fuscous prevails dorsally, the luteous laterally; there is an interrupted and irregular broad rufo-luteous mediodorsal band on the thoracic segments, and the inferior margins of at least the pronotum are bordered with luteous, but the other luteous markings are mostly in the form of rather irregularly scattered, more or less irregularly confluent small round spots, often becoming blotches of great irregularity on the thorax; legs dull luteous, the femora infuscated especially apically and the hind femora heavily marked in a scalariform pattern as well as apically annulate with fuscous. The antennæ are slender and apparently about twice as long as the body, and the legs slender and moderately long. Fore femora not stouter than the middle pair, varying greatly in length in the sexes, in the male being only a little less than half as long as the hind femora and more than a third as long again as the pronotum, in the female very much less than half as long as the hind femora, and not a fifth longer than the pronotum, the inner carina with two spines, at least the subapical rather long. Middle femora with 2–4 spines on the front carina and on the hind carina 1–2 spines besides a not very long genicular spine. Hind femora about as long as the body, a little more than twice (♂) or considerably more than two and a half times (♀) as long as the fore femora, slender and very gradually tapering, about three and three quarters times as long as broad, the apical fifth subequal, with no raised points upon the surface, the outer carina minutely and inequidistantly spinulate or subserrate, in the female the serrations much subdued, the inner carina similarly but more finely armed in both sexes, the intervening sulcus narrow. Hind tibiæ straight, scarcely longer than the femora, slender, armed beneath with a single preapical spine besides the apical pair; spurs subalternate, the basal about the end of the proximal fourth of the tibia, less than twice as long as the tibial depth, set at an angle of 70–80° with the tibia and divaricating about 90° (♂) or 150–170° (♀), their tips incurved; inner middle calcaria *distinctly longer than the outer, much more than twice as long as the* others or as the spurs and as long as the first tarsal joint. Hind tarsi much less than half as long as the tibiæ, the first joint as long as the rest together, the second more than twice as long as the third and nearly as long as the fourth. Cerci short, being hardly longer than half the femoral breadth. Extremity of the abdomen roundly truncate in the male. Ovipositor straight beneath, the upper margin broadly arcuate, nearly two thirds as long as the hind femora, tapering in basal, equal and slender in distal half, the tip upcurved and finely acuminate, the teeth of the inner valves aculeate, only the last one arcuate.

Length of body, ♂ 12 mm., ♀ 16 mm.; pronotum, ♂ 3.5 mm., ♀ 5.25 mm.; fore femora, ♂ 5 mm., ♀ 6.1 mm.; hind femora, ♂ 10.9 mm., ♀ 16 mm.; hind tibiæ, ♂ 11 mm., ♀ 16.3 mm.; ovipositor, 10.5 mm.

3 ♂, 7 ♀. Dallas and Crawford Cos., Iowa (J. A. Allen); West Point, Nebr (L. Bruner).

13. CEUTHOPHILUS TERRESTRIS, sp. nov.

Rhaphidophora lapidicola Scudd.!, Proc. Bost. Soc. Nat. Hist., viii. 7 (1861).

Ceuthophilus lapidicolus Scudd.!, Bost. Journ. Nat. Hist., vii. 435 (1862); Walk., Catal. Derm. Salt. Brit. Mus., i. 201 (1869); Glov., Ill. N. A. Entom., Orth., pl. 7, figs. 4, 5 (1872); Prov., Nat. Canad., viii. 75 (1876); Ril., Stand. Nat. Hist., ii. 184 (1884); Smith, Cat. Ins. N. J., 409 (1890); Osb.?, Proc. Iowa Acad. Sc., ii. 119 (1892); Blatchl., Proc. Ind. Acad. Sc., 1892, 147–148 (1894).

Phalangopsis lapidicola Bess., Rep. Iowa Agric. Coll., vii. 206 (1877).

Glabrous, mottled with luteous and blackish fuscous, both colors varying in tint in different individuals; there is often, but not always, a mediodorsal light stripe on the thorax bordered by dark tints, and the lower portions of the sides are always lighter than the rest; the intervening portions of the thorax may be described as fuscous, heavily sprinkled and blotched irregularly with luteous, sometimes one, sometimes the other prevailing; on the abdomen the darker colors prevail and the lighter appear as a tolerably regular and profuse sprinkling of often confluent luteous dots, most abundant on the posterior portions of the segments; the hind femora have the usual markings, and are feebly and narrowly infuscate apically. The antennæ are slender, fully twice as long as the body, the legs moderately short. Fore femora not stouter than the middle pair, a third longer than the pronotum and distinctly less than half as long as the hind femora, the inner carina with a long preapical spine sometimes accompanied by a shorter one. Middle femora with 1–2 spines on the front carina besides a preapical spine, and on the hind carina usually two spines besides the genicular spine. Hind femora somewhat shorter than the body, considerably more than twice as long as the fore femora, less than three times as long as broad, the swollen portion pretty stout, hardly more than the distal sixth of equal width, with a few feebly raised points on the upper apical portion of the inner side only, the outer carina delicately uniformly and densely serrate throughout (♂) or with a few apical obscure serrations (♀), the inner carina similar. Hind tibiæ straight in both sexes, rather stout in the male, scarcely exceeding the femora in length, armed beneath with a preapical spine besides the apical pair; spurs subopposite, the basal beyond the end of the proximal third of the tibia, hardly or no longer than the tibial depth, set at an angle of 45° with the tibia and divaricating 90–100°, their tips incurved; inner middle calcaria somewhat longer than the outer, twice as long as the others or as the spurs, but not so long as the first tarsal joint. Hind tarsi two fifths the length of the tibiæ, the first joint nearly as long as the rest together, the second twice as long as the third and with it longer than the fourth. Cerci rather slender throughout, tapering, pointed, as long as the femoral breadth. Ovipositor less than three fifths as long as the hind femora, gently tapering in the proximal half, equal and not very slender in the distal half, the tip upturned a little and pointed at an angle of 45°, the teeth of the inner valves sharp but not aculeate.

Length of body, ♂ 13 mm., ♀ 15 mm.; pronotum, ♂ ♀ 4 mm.; fore femora, ♂ 5.3 mm., ♀ 5.6 mm.; hind femora, ♂ 12.3 mm., ♀ 12.5 mm.; hind tibiæ, ♂ 12.5 mm., ♀ 12.75 mm.; ovipositor, 7 mm.

11 ♂, 5 ♀. North Red River, P. R. Uhler; Chateaugay Lake, Adirondack, N. Y., 2,000′, F. C. Bowditch; New Hampshire; Moosehead Lake, Me.; Cambridge and Lowell, Mass., S. Henshaw; Maryland, P. R. Uhler. Specimens in the Museum of Comparative Zoölogy are from Anticosti (Verrill), from Norway (Smith), Bethel (Miss Edwards), and Gorham, Me., and from Nahant and Malden, Mass. (A. Agassiz). It is also reported, partly no doubt by mistake for other species, from Iowa (Bessey, Osborn), Penn., Md., Geo., Ind. (Walker), Canada (Provancher), New Jersey (Smith), Indiana (Blatchley), and Nebraska (Bruner).

14. Ceuthophilus celatus, sp. nov.

Body blackish fuscous, glabrous, liberally sprinkled with luteo-testaceous giving it a speckled appearance in best marked specimens; some of these spots or dots are clustered in a more or less conspicuous mediodorsal stripe, while others margin subequidistantly the posterior border of all the abdominal segments or are submarginal; on the pronotum and to a less degree on the meso- and metanotum they are liable to coalesce and form vague and irregular patches and blotches; the fore and middle legs are luteous, more or less infuscated especially at the distal ends of the femora; hind femora brownish fuscous, often with an olivaceous tint, the scalariform markings nearly obsolete. Antennæ very slender, about twice the length of the body, the legs rather short. Fore femora no stouter than the middle femora, about a third (♂) or a fourth (♀) longer than the pronotum, and much less than half as long as the hind femora, the inner carina with a subapical spine sometimes accompanied by a few others near it. Middle femora with a subapical spine sometimes accompanied by one or two others on the front carina, and on the hind carina a not very long genicular spine sometimes accompanied by two others. Hind femora rather slender, tapering almost regularly, about three and a half times as long as broad, considerably more than twice as long as the fore femora, with no raised points upon the surface, the outer carina very finely denticulate (♂) or wholly or almost wholly unarmed (♀), the inner carina feebly and very finely serratulate, the intervening sulcus narrow. Hind tibiæ straight in both sexes, a little longer than the femora, slender, armed beneath with a single subapical spine besides the apical pair; spurs opposite or subopposite, the basal at the end of the proximal fourth of the tibia, no longer than the tibial depth, set at an angle of about 45° with the tibia and divaricating about 60°; inner middle calcaria considerably longer than the outer, more than twice as long as the others or as the spurs, but shorter than the first tarsal joint. Hind tarsi a little less than half as long as the tibia, the first joint scarcely as long as the rest together, the second much more than twice as long as the third and with it longer than the fourth. Cerci slight, tapering regularly, about three fourths as long as the femoral breadth. Ovipositor straight, tapering on the proximal, slender and equal on the distal half, somewhat more than half as long as the hind femora, the tip very gradually attenuated and very slightly upcurved, not very finely pointed, the inner valves rather feebly crenulate.

Length of body, ♂ 9 mm., ♀ 13 mm.; pronotum, ♂ 3 mm., ♀ 3.5

mm.; fore femora, ♂ 4 mm., ♀ 4.25 mm.; hind femora, ♂ 9 mm., ♀ 10 mm.; hind tibiæ, ♂ 9.5 mm., ♀ 10.75 mm.; ovipositor, 6 mm.

3 ♂, 5 ♀. Behrens, Shaster County, Cal., San Francisco, Cal., Los Angeles, Cal., Coquillett, all from L. Bruner; and Siskiyou, Placer, and Los Angeles Counties, Cal., mostly from Riley's collection (U. S. Nat. Mus.).

15. CEUTHOPHILUS BREVIPES.

Ceuthophilus brevipes Scudd.!, Bost. Journ. Nat. Hist., vii. 434 (1862); Walk., Cat. Derm. Salt. Brit. Mus., i. 201 (1869); Prov., Nat. Canad., viii. 75 (1876); Fern., Orth. N. Engl., 19 (1888); Blatchl.!, Proc. Ind. Acad. Sc., 1892, 148 (1894).

Dull fuliginous brown, but glabrous, marked with very dull and pale luteous dots, occasionally somewhat confluent; there is sometimes, but rarely, a mediodorsal luteous stripe on the pronotum; the dots are generally a little elongate and margin the segments posteriorly, often turned obliquely inward and when accompanied by other dots in advance these arranged to give an added obliquity to their general course; the pronotum is more or less marmorate with dull luteous; the legs have the general tone of the body and the hind femora the usual markings of the genus, the darker colors generally the more extensive, but the pattern obscured apically so that the distal extremity of the femora, including more than the geniculation, is more or less deeply infuscated. The antennæ are stout at base but immediately become slender and are at least twice as long as the body. The legs are short and rather slender. Fore femora no stouter than the middle femora, a third longer than the pronotum and about half as long as the hind femora, the inner carina with a subapical spine. Middle femora with a subapical spine on the front carina and on the hind carina 1–2 spines, sometimes wanting in the ♀, besides a fairly long genicular spine. Hind femora moderately stout and plump, regularly tapering, about three and a half times longer than broad, the distal fifth equal, the surface with no raised points, both carinæ sparsely and finely serrate in the ♂, almost unarmed in the ♀, the intervening sulcus of moderate breadth and V-shaped. Hind tibiæ considerably longer than the femora, unusually slender, straight in both sexes, armed beneath with two preapical spines besides the apical pair; spurs subopposite, the basal at the end of the proximal fourth of the tibia, nearly half as long again as the tibial depth, set at an angle of 40–45° with the tibia and divaricating about 135°, their tips incurved; inner middle calcaria considerably longer than the outer, nearly twice as long as the others or as the spurs, but much shorter than the first tarsal joint. Hind tarsi about two fifths the length of the tibia, the first joint shorter than the others together, the second twice as long as the third and with it as long as the fourth. Cerci rather slender, regularly tapering, slightly longer than the femoral breadth. Ovipositor gently tapering on proximal, equal on distal half, rather slender, very slightly arcuate, two thirds the length of the hind femora, the tip acute but not produced, the armature of the inner valves a dull and nearly obsolete serration.

Length of body, ♂ 14 mm., ♀ 15.5 mm.; pronotum, ♂ 3.9 mm., ♀ 4.5 mm.; fore femora, ♂ 5.5 mm., ♀ 6 mm.; hind femora, ♂ 11 mm., ♀ 13 mm.; hind tibiæ, ♂ 12 mm., ♀ 13.5 mm.; ovipositor, 8.4 mm.

3 ♂, 3 ♀. Grand Menan Isl., Me., A. E. Verrill; Vigo Co., Ind., October, Blatchley. Specimens are in the Museum of Comparative Zoölogy from St. Johns, N. B.

Provancher gives it from Canada with a query, and it appears, but wrongly, in Bruner's list of the Orthoptera of Nebraska (Publ. Nebr. Acad. Sc., iii. 32, 1893).

16. CEUTHOPHILUS LAPIDICOLA.

Phalangopsis lapidicola Burm., Handb. d. Ent., ii. 723 (1838).

Locusta (Rhaphidophorus) lapidicola De Haan, Bijdr. Kenn. Orth., 178 (1842).

Body glabrous, blackish above and on upper part of sides, with a very broad dark rufous mediodorsal stripe, narrowing on the abdomen and disappearing in the middle of the same, the black portions sprinkled, especially on the abdomen where it covers all the sides, with rufo-luteous dots or small roundish spots, the lower portion of the sides of the thorax and especially of the pronotum luteous, flecked and clouded to a greater or less degree with fuscous; antennæ fuscous, very distantly and narrowly annulated with luteous; legs luteous, infuscated more or less — and in this very variable — especially at the distal extremity of the femora, the hind femora almost wholly blackish fuscous externally, flecked, streaked, or stained, especially below, with sordid luteous. The antennæ are very slender and at least three and a half times as long as the body, and the legs slender and pretty long. Fore femora barely stouter in the basal half than the middle femora, somewhat less than half as long as the hind femora, nearly a half (♂) or almost a third (♀) longer than the pronotum, the inner carina with two rather short spines. Middle femora with 2–3 rather short spines on the front carina and on the hind carina two very feeble spines besides a moderately long genicular spine. Hind femora about as long as the body, somewhat more than twice as long as the fore femora, rather slender, being fully three and a half times as long as broad, the distal third to fourth subequal, the inner surface above and beyond the middle with three or four distant raised points, both carinæ feebly spinulate in the distal half, the outer more strongly than the inner in the male, the reverse in the female which as a whole is a little more feebly armed, the intervening sulcus rather narrow. Hind tibiæ straight in both sexes, of the same length as the femora, armed beneath with 1–2 subapical spines besides the apical pair; spurs subopposite, the basal before the end of the proximal third of the tibia, with sometimes a supplementary spur still farther toward the base, fully half as long again as the tibial depth, set at an angle of about 70° with the tibia, and divaricating about 160°, the apical third incurved; inner middle calcaria considerably longer than the outer, fully twice as long as the others or as the spurs and scarcely shorter than the first tarsal joint. Hind tarsi two fifths as long as the tibiæ, the first joint somewhat shorter than the rest combined, the second more than twice as long as the third and with it about as long as the fourth. Cerci rather slender, scarcely shorter than the femoral breadth. Ovipositor a little less than two thirds as long as the hind femora, straight, feebly tapering on the basal third, equal and moderately broad beyond, the tip a little upturned and acuminate (about 35°), the teeth not long, aculeate.

Length of body, ♂ ♀ 21 mm.; antennæ (est.), ♂ 75+ mm., ♀ 68+ mm.; pronotum, ♂ 6.5 mm., ♀ 7 mm.; fore femora, ♂ 9.5 mm., ♀ 8.9 mm.; hind femora and tibiæ, ♂ 20.25 mm., ♀ 20.4 mm.; ovipositor, 12.75 mm.

1 ♂, 2 ♀, and 3 immature specimens, N. Carolina. Morrison (Coll. Henshaw, Bruner). A ♀ from Pennsylvania is in the Museum of Comparative Zoölogy, and a ♀ without locality in the U. S. National Museum.

Burmeister's *Phal. lapidicola* came from Virginia and South Carolina. The present species is the only one known to me from the Southern Atlantic States which completely or approximately agrees with his description, the species formerly referred by me and others to this being a Northern form to which the description poorly fits, and that described by Brunner under this name is a very different insect.

17. CEUTHOPHILUS ARIZONENSIS, sp. nov.

Pallid luteous, so heavily infuscated that behind the pronotum there is only left a single series of luteous spots on each side, which on the meso- and metanotum are transverse oval and rather large, and on the abdomen are transverse anterior stripes, sometimes confluent with those of the opposite side; the pronotum is mostly fuscous, deepest around the margin, more or less dotted and vermiculate with luteous elsewhere, there being commonly a transverse row of dots bordering the anterior fuscous margin, and the disk on either side more or less heavily blotched with the same; the legs are fuscous, varying in depth in different individuals, the hind femora generally with sufficiently conspicuous scalariform markings. The antennæ are very slender and fully three times as long as the body, and the legs are slender but not very long. Fore femora slightly stouter than the middle femora, a third longer than the pronotum and half as long as the hind femora, the inner carina with one or two spines. Middle femora with 1–3 spines on the front carina, and the hind carina generally unarmed except for a slight genicular spine, but sometimes with as many as three other minute spines. Hind femora nearly as long as the body, twice the length of the fore femora, moderately slender, being a little less than three and a half times longer than broad, gradually diminishing in size and yet with the distal fourth subequal, the surface with no raised points, the outer carina with only a few raised points, mostly on the distal half, the inner carina with most minute but sharp distant spinules, the intervening sulcus narrow. Hind tibiæ scarcely longer than the femora, straight in both sexes, very slender, armed beneath with a single preapical spine besides the apical pair; spurs nearly opposite, the basal beyond the end of the proximal third of the tibia, about as long as the tibial depth, set at an angle of from 35–40° with the tibia and generally divaricating about 70–80° (one example about 100°), their tips incurved; inner middle calcaria a little longer than the outer, fully twice as long as the others or as the spurs, but much shorter than the first tarsal joint. Hind tarsi less than half as long as the tibiæ, the first joint fully as long as the rest combined, the second twice as long as the third and with it as long as the fourth. Cerci stout on the proximal, slender on the distal half, nearly as long as the femoral breadth. Ovipositor four fifths the length of the hind femora, slender, nearly straight, tapering slightly, the tip finely pointed at an angle of about 30° and barely upturned, the armature of the inner valves aculeate, only the terminal arcuate.

Length of body, ♂ 8 mm., ♀ 11.5 mm.; pronotum, ♂ 2.7 mm., ♀ 3.75 mm.; fore femora, ♂ 3.75 mm., ♀ 5 mm.; hind femora, ♂ 7.5 mm., ♀ 10 mm.; hind tibiæ, ♂ 8 mm., ♀ 10.2 mm.; ovipositor, 8 mm.

3 ♂, 9 ♀. St. George, Utah, April 1–12, E. Palmer; Prescott Mt. district, Central Arizona, E. Palmer. One specimen was collected by Xantus, locality not mentioned but not improbably Cape St. Lucas, Lower California. In the U. S. National Museum are 3 ♂, 1 ♀, from Ft. Wingate, N. Mex. (Shufeldt), in the Riley collection.

18. CEUTHOPHILUS UNIFORMIS, sp. nov.

Ceuthophilus pallidus Scudd. !, Bull. U. S. Geol. Geogr. Surv. Terr., ii. 261 (1876); Id. !, Ann. Rep. Geogr. Surv. West 100th Mer., 1876, 279; Brun. ?, Bull. Washb. Coll., i. 126 (1885), i. 194–195 (1886); Id. ?, Publ. Nebr. Acad. Sc., iii. 32 (1893).

Smoky luteo-testaceous with a slight olivaceous tinge, glabrous, marked more or less deeply with fuscous along the posterior margins of the segments and generally along the anterior margin of the pronotum; in this posterior infuscation are indistinct dots of luteous in a transverse series; generally there is also a mediodorsal luteous line over all the segments but deepest and broadest on the pronotum, which is also laterally irregularly streaked, clouded, or blotched with luteous; beyond the lighter more luteous bases of the femora, the legs are of the body color, but the hind femora are considerably infuscated in a scalariform pattern, apically confluent. The antennæ are slender and nearly or quite three times the length of the body and the legs are moderately short. Fore femora no stouter than the middle femora, more than a third (♂) or less than a fourth (♀) longer than the pronotum and somewhat less than half as long as the hind femora, the inner carina armed only with a subapical spine. Middle femora with two spines on the front carina, and on the hind carina 2–3 (♀) or 3–4 (♂) spines besides a not very long genicular spine. Hind femora nearly as long as (♂) or much shorter than (♀) the body, a little more than twice as long as the fore femora especially in the ♀, pretty stout, in the ♂ being but a little more than two and a half times longer than broad, though in the ♀ fully three and a quarter times as long as broad, with no raised points on the surface, or at most four or five scattered insignificant ones on the inner surface in the ♂, the outer carina with a few spinous points on the distal half, the inner carina similarly armed but in the ♂ weaker, the intervening sulcus narrow. Hind tibiæ scarcely or no longer than the femora, straight in both sexes, slender, armed beneath with a single subapical spine besides the apical pair; spurs almost opposite, the basal rather beyond the end of the proximal third of the tibia, scarcely longer (♂) or a little longer (♀) than the tibial depth, set at an angle of about 45° with the tibia and divaricating 70–90°, their tips incurved; inner middle calcaria distinctly longer than the outer, twice as long as the others or as the spurs, but distinctly shorter than the first tarsal joint. Hind tarsi nearly half as long as the tibiæ, the first joint fully (♂) or nearly (♀) as long as the rest taken together, the second more than twice as long as the third and nearly as long as the fourth. Cerci rather stout tapering from before the middle, shorter than the femoral breadth. Ovipositor nearly twice as long as the fore femora and not very much shorter than the hind tibiæ, beyond the extreme very slightly swollen base slender and subequal but gently tapering, slightly arcuate in the distal half, the extreme tip produced to a very fine scarcely upturned point, the armature including the apical members consisting of sharp minute reversed serrations hardly apparent until mature.

Length of body, ♂ 10.7 mm., ♀ 16 mm.; pronotum, ♂ 3.25 mm., ♀ 4.1 mm.; fore femora, ♂ 5 mm., ♀ 4.9 mm.; hind femora, ♂ 10.2 mm., ♀ 11 mm.; hind tibiæ, ♂ 10.5 mm., ♀ 11 mm.; ovipositor, 9.4 mm.

5 ♂, 9 ♀. Plains of Northern New Mexico, eastern slope, October 14; Beaver Brook, Col., 6,000′, July 11, S. H. Scudder; Empire City, Col., E. Palmer. It has also been reported from Southern Colorado, Manitou and Idaho, Col. (Scudder), Western Nebraska, and Topeka and Berks Co., Kans. (Bruner).

19. CEUTHOPHILUS HEROS, sp. nov.

Body castaneous, so heavily marked with black or blackish fuscous as to appear rather as black marked with castaneous; the latter appears on the pronotum only in a very broad mediodorsal stripe of unequal width, an impure blotch in the middle of the sides usually connected with the former, and an inferior edging sometimes expanding anteriorly; in younger specimens, however, it extends over nearly all the surface; on the meso- and metanotum it margins the segments anteriorly except below, separated from the black irregularly, and extends mediodorsally across the segments; on the abdomen it appears as small spots dotting the surface and merging along the anterior margins; the antennæ are pale fuscous obscurely and distantly annulated with luteous; the legs are castaneous, more or less infuscated, the hind femora externally marked heavily with fuscous in a scalariform pattern, with a broad obscure castaneous annulation well before the genicular lobes. The antennæ are slender and exceedingly long, about four times as long as the body, and the legs are very long though only moderately slender. Fore femora no stouter than the middle femora, a little less than half as long as the hind femora, and rather more (♂) or rather less (♀) than three fourths as long again as the pronotum, the inner carina with 2–3 spines. Middle femora with similar spines on the front carina and on the hind carina a couple of similar spines besides a not very long genicular spine. Hind femora fully as long as the body, a little more than twice as long as the fore femora, the basal portion stout and swollen but delicately tapering so that nearly or in the female quite the apical third is subequal, and the whole is four times as long as broad, the upper edge of the inner surface with 4–5 distant raised points, the outer carina with about ten sub-equal spines, the longest much shorter than the tibial spurs (♂), or with about six slight and distant recumbent spines (♀), the inner carina rather bluntly denticulate, distantly in the outer half (♂) or like the outer carina but more closely denticulate (♀), the intervening sulcus narrow. Hind tibiæ barely arcuate at base (♂) or straight (♀), a very little longer than the femora, armed beneath with 1–2 subapical spines besides the apical pair; spurs subopposite, the basal at the end of the proximal third of the tibia, a little longer than the tibial depth, set at an angle of about 60° with the tibia and divaricating about 130° (♂) or 150–170° (♀), incurved at tip; inner middle calcaria a little longer than the outer, twice as long as the others or as the spurs, and as long as the first tarsal joint. Hind tarsi two fifths as long as the tibiæ, the first joint much shorter than the rest together, the second nearly three times as long as the third and with it fully as long as the fourth. Cerci slender, nearly half as long again as the femoral breadth. Ovipositor three fifths as long as the hind femora, straight, tapering and not very stout in the basal, slender and equal in the apical half, the apex obliquely truncate, upturned, and acuminate but not much produced, the teeth of the inner valves rather short and aculeate.

Length of body, ♂ 23.5 mm., ♀ 21 mm.; antennæ, ♂ 85 mm., ♀ 92 mm.; pronotum, ♂ 6.25 mm., ♀ 7.2 mm.; fore femora, ♂ 11.5 mm., ♀ 12 mm.; hind femora, ♂ 24 mm., ♀ 25 mm.; hind tibiæ, ♂ 25.5 mm., ♀ 26 mm.; ovipositor, 15 mm.

3 ♂, 2 ♀. North Carolina, H. K. Morrison; over two hundred were found in one old hollow tree when it was felled. 2 ♂ and 2 ♀.

of what is apparently the same species, but smaller, are in the U. S. National Museum from Washington, D. C.

20. CEUTHOPHILUS UHLERI.

Ceuthophilus uhleri Scudd.!, Bost. Journ. Nat. Hist., vii. 435 (1862); Walk., Catal. Derm. Salt. Brit. Mus., i. 201 (1869): Glov., Ill. N. A. Ent., Orth., pl. 8, fig. 8 (1872); Riley, Stand. Nat. Hist., ii. 184 (1884); Brunn., Monogr. Stenop., 64–65, fig. 33b (1888); Smith, Catal. Ins. N. J., 409 (1890).

Ceuthophilus latisulcus Blachl.!, Proc. Ind. Acad. Sc., 1892, 146 (1894).

Dull luteo- or rufo-testaceous, very heavily flecked with dark fuscous so as to produce a tolerably uniform mottled appearance, ordinarily a little more open than elsewhere in a narrow mediodorsal streak on the pronotum, and in the tolerably clear luteous or pallid luteous of the inferior margin of the descending thoracic lobes; the flecking is made up of small more or less confluent dots, which assume a certain longitudinal regularity on the abdomen only; legs varying from luteous to testaceous, more or less infuscated, especially on the apical portions of the femora and in the distinct and heavy scalariform markings of the hind femora. The antennæ are moderately stout in the basal, but in the apical half very slender, apparently only a little more than twice the length of the body, the legs moderately long. Fore femora no stouter than the hind femora, much less than half as long as the hind femora, but considerably more than a third longer than the pronotum in the ♂ though only a fourth longer in the ♀, the inner carina with 2–3 spines, the subapical not much longer than the others. Middle femora with the front carina as in the fore femora, the hind carina armed with 1–3 spines besides a moderately long genicular spine. Hind femora longer (♂) or shorter (♀) than the body, considerably more than twice as long as the fore femora (at least a third more in the male), stout, the apical third or fourth subequal, about three and a third times as long as broad in the male, the darker portions of the surface of the apical half of the femora and the upper portion of the inner side rather heavily (♂) or very sparsely (♀) scabrous with raised points, the outer carina armed with 7–8 unequal inequidistant coarse irregular arcuate spines, the largest (just beyond the middle) as long as but much stouter than the tibial spurs (♂) or almost entirely unarmed but for some 3–4 raised points (♀), the inner carina with about sixteen small inequidistant coarse spinules covering the whole length (♂) or a few slight ones only on the apical fourth of the femora (♀), the intervening sulcus exceptionally broad. Hind tibiæ faintly and irregularly sinuous (♂) or straight (♀), distinctly longer than the femora, slender, armed beneath with 1–2 subapical spines besides the apical pair; spurs subopposite, the basal at or a little beyond the end of the proximal fourth of the tibia, a little longer than the tibial depth, set at an angle of about 35° with the tibia and divaricating 80°–90°, the apical half incurved; inner middle calcaria much longer than the outer, more than twice as long as the others or as the spurs, but scarcely so long as the first tarsal joint. Hind tarsi two fifths as long as the tibiæ, the first joint about as long as the rest together, the second nearly three times as long as the third and with it fully as long as the fourth. Cerci rather stout, shorter than the femoral breadth. Ovipositor only slightly enlarged at base, the distal two thirds equal but not very slender, straight, almost two thirds as long as the hind femora, the tip considerably upcurved and finely acuminate, the teeth of the inner valves triangular, increasing in length apically, only the terminal arcuate.

Length of body, ♂ ♀ 15.5 mm.; antennæ, ♀ 32+ mm.; pronotum, ♂ 5.1 mm., ♀ 4.6 mm.; fore femora, ♂ 7.35 mm., ♀ 5.75 mm.; hind femora, ♂ 17.75 mm., ♀ 13 mm.; hind tibiæ, ♂ 18.5 mm., ♀ 14 mm.; ovipositor, 8.25 mm.

7♂, 3♀. Maryland (P. R. Uhler); Middle States (R. Osten Sacken); Vigo Co., Ind., (W. S. Blatchley); Georgia. It is also reported from New Jersey (Smith) and Tennessee (Brunner). Bruner quotes it doubtfully among Nebraska Orthoptera, but I do not know to what species he refers.

Easily confounded with *C. blatchleyi.*

21. CEUTHOPHILUS BLATCHLEYI.

Ceuthophilus uhleri Blatchl.!, Proc. Ind. Acad. Sc., 1892, 144–145 (1894).

In color and markings this species is indistinguishable from *C. uhleri.* The legs and especially the hind femora are slenderer. Fore femora no stouter than the hind femora, much less than half as long as the fore femora, fully a third (♂) or scarcely a fourth (♀) as long again as the pronotum, the inner carina with 2–3 spines, the subapical long. Middle femora armed on the front carina much as in the fore legs, the hind carina with a long genicular spine sometimes accompanied by 1–3 other spines, often minute. Hind femora nearly two and a half times as long as the fore femora, longer than the body in both sexes, slender and tapering, nearly the apical third subequal, three and a half times as long as broad in the male and fully three and three quarters in the female, the upper portion of the apical half of the inner surface and to a less degree the upper surface near it with numerous raised points, but not so pronounced as in *C. uhleri*, the outer carina armed exactly as there but with wider intervals between the larger spines and the spines less stout (♂), or with 2–3 scarcely noticeable spinules near the apex (♀), the inner carina with about 12–14 serrulations unequally placed, slight, less numerous and distinctly slighter in the female than in the male, the intervening sulcus only moderately broad. Hind tibiæ with a hardly noticeable arcuation or sinuation in the male, hardly (♂) or much (♀) longer than the femora, slender, armed beneath with two median subapical spines besides the apical pair; spurs subalternate, the basal at about the end of the proximal fourth of the tibia, considerably longer than the tibial depth, set at an angle of about 35° with the tibia and divaricating 98°–100°, their apical fourth incurved; inner middle calcaria considerably longer than the outer, more than twice as long as the others or as the spurs, and fully as long as the first tarsal joint. Hind tarsi about two fifths as long as the tibiæ, the first joint longer than the other joints together, the second much more than twice as long as the third and with it longer than the fourth. Cerci stout at base, beyond slender, about as long as the femoral breadth. Ovipositor straight, almost two thirds as long as the hind femora, very little enlarged at base, tapering almost throughout but very gently, the tip upturned a little and finely acuminate, the armature as in *C. uhleri*.

Length of body, ♂ 13.5 mm., ♀ 13 mm.; pronotum, ♂ 4.7 mm., ♀ 4.5 mm.; fore femora, ♂ 6.4 mm., ♀ 5.5 mm.; hind femora, ♂ 15.75 mm., ♀ 13.5 mm.; hind tibiæ, ♂ ♀ 16.25 mm.; ovipositor, 8.5 mm.

2 ♂, 2 ♀. Vigo Co., Indiana (W. S. Blatchley); also from New York, Riley (U. S. Nat. Mus.).

Distinguishable from *C. uhleri* by the slightly different and weaker armature of the carinæ of the hind femora, but especially by the slenderer hind femora, and the narrower inferior sulcus of the same. I probably led Mr. Blatchley into his pardonable error by determining this for him as *C. uhleri*.

22. CEUTHOPHILUS SPINOSUS.

Ceuthophilus lapidicola Brunn., Monogr. Stenop., 63–64 (1888).

Body dark fusco-castaneous, glabrous, with irregular luteous spots and blotches covering a considerable portion of the thoracic segments; the lower edges of the sides of the thoracic segments are sordid luteous and the abdomen is mostly marked with alternate longitudinal bars of luteous and fuscous, the latter prevailing dorsally; legs luteo-castaneous, the hind femora distinctly but not heavily marked with fuscous in scalariform patterns. Legs not very long. Fore femora broader basally than the middle femora, much less than half as long as the fore femora, and only a fifth longer than the pronotum, the inner carina with a short spine besides a long preapical spine. Middle femora armed with three spines on the front carina, the preapical very long, the hind carina with only a couple of very short spines besides the long genicular spine. Hind femora longer than the body, two and a half times as long as the fore femora, very stout but with the distal portion so produced that the apical fourth is equal, the whole three times as long as broad, the surface covered everywhere on the darker portions, but especially on the stouter part of the femora beyond the middle and within as well as without, with raised points closely crowded, the outer carina elevated, armed in the middle third with a series of about five spines, sometimes inequidistant, distally increasing in length, the last and to some extent the others bent-arcuate, about as long as the tibial spurs but coarser, followed by a rapid narrowing of the femora and on this narrow portion by 4–5 minute serrulations, the inner carina pretty regularly and minutely but not closely spinulate, the intervening sulcus broad. Hind tibiæ feebly arcuate, somewhat longer than the femora, armed beneath with a single subapical spine besides the apical pair; spurs subopposite, the basal at the end of the proximal fourth of the tibia, half as long again as the tibial depth, set at an angle of about 45° with the tibia and divaricating 90–100°, their tips incurved; inner middle calcaria considerably longer than the outer, fully twice as long as the others or as the spurs, and as long as the first tarsal joint. Hind tarsi about two fifths as long as the tibiæ, the first joint hardly as long as the rest together, the second twice as long as the third, but with it scarcely as long as the fourth. Cerci moderately slender, rather short, probably little exceeding in length the femoral breadth.

Length of body, 13 mm.; pronotum, 5 mm.; fore femora, 6 mm.; hind femora, 15 mm.; hind tibiæ, 16 mm.

1 ♂. Georgia.

This species is very closely related to *C. uhleri*, differing in its markings, which are less sprinkled, and in the more pronounced spinulations of the hind femoral carinæ in the male.

23. CEUTHOPHILUS CÆCUS, sp. nov.

Body glabrous, blackish fuscous above, pallid and more or less sordid luteous on the lower portion of the sides, with a mediodorsal rufo-luteous line and dotted above faintly and rather sparsely with rufo-luteous, some of the dots broadening the mediodorsal line, others next the luteous sides becoming larger and sometimes more distinctly luteous, and on the abdomen often becoming oblique dashes; the very edge of the inferior margins of the thoracic lobes castaneous; antennæ fusco-luteous; legs luteous, more or less infuscated, the hind femora luteo-castaneous, with heavy and distinct blackish fuscous scalariform markings, much heavier on distal than proximal half. The antennæ are slender and about three times the length of the body, the legs moderately short. Fore femora slightly broader than the middle femora, very much less than half as long as the hind femora and at most (♂) only a fourth longer than the pronotum, the inner carina with 2–3 spines, at least the preapical long. Middle femora with 2–4 long spines, the preapical very long, on the front carina, the hind carina with 0–2 short spines besides a very long genicular spine. Hind femora as long as the body, two and a half times as long as the fore femora, very stout, scarcely more than three times as long as broad, the stout portion rapidly tapering so that the apical fourth is subequal, the inner surface of the male with a cluster of raised points beyond the middle, above, the outer carina elevated, having on the middle third a row of increasingly larger spinules, the largest still very much shorter than the tibial spurs, followed distally by half a dozen minute and equal spinules (♂) or unarmed (♀), the inner carina with a few small subequal spinules in the distal half, smaller and sparser in the ♀ than in the ♂, the intervening sulcus broad. Hind tibiæ straight in both sexes, a little longer than the femora, armed beneath with a single preapical spine besides the apical pair; spurs subopposite, the basal not much beyond the end of the proximal fourth of the tibia, almost twice as long as the tibial depth, set at an angle of 35–45° with the tibia, divaricating about 130° at least in the ♀, their tips considerably incurved; inner middle calcaria considerably longer than the outer, nearly twice as long as the others or as the spurs, and about as long as the first tarsal joint. Hind tarsi nearly two fifths as long as the tibiæ, the first joint fully as long as the rest together, the second three times as long as the third and with it fully as long as the fourth. Cerci moderately slender, bluntly pointed, much shorter than the femoral breadth. Ovipositor scarcely longer than the fore femora, feebly arcuate, the base moderately stout, the distal three fifths equal and moderately slender, the tip considerably upturned and very acuminate.

Length of body, ♂ 11.5 mm., ♀ 10 mm.; antennæ (est.), ♂ 32 mm., ♀ 31 mm.; pronotum, ♂ 4 mm., ♀ 4.25 mm.; fore femora, ♂ 5 mm., ♀ 4.5 mm.; hind femora, ♂ 12.5 mm., ♀ 11.25 mm.; hind tibiæ, ♂ 13.5 mm., ♀ 11.7 mm.; ovipositor, 4.75 mm.

1 ♂, 2 ♀. Lexington, Ky., June 28, S. Garman. A single imperfect ♂ in the National Museum without locality (Missouri?) probably belongs to this species.

24. CEUTHOPHILUS NIGRICANS, sp. nov.

Body glabrous, blackish fuscous with obscure rufo-luteous markings, becoming pallid luteous and more distinct on the abdomen; they consist almost wholly of a sprinkling of small roundish spots and dots, more profuse and elongated on the abdomen, but there is besides a very obscure mediodorsal line or stripe on the pronotum; excepting on the under surface of the femora, the femora and tibiæ are dark fuliginous and the outer side of the hind femora very dark castaneous, heavily infuscated in the apical half, blackish at tip, and with deep and heavy fuscous scalariform markings. The antennæ are slender and at least in the basal portion blackish fuscous, and the legs are rather short, though the hind legs are relatively much longer in the female than in the male. Fore femora not stouter than the middle femora, much less than half as long as the hind femora, particularly in the female, and very little longer than the pronotum, the inner carina with one or two short spines. Middle femora similarly armed on the front carina, the hind carina with one or two spines besides a short genicular spine. Hind femora shorter (♂) or longer (♀) than the body, somewhat more than twice (♂) or about three times (♀) as long as the fore femora, in the male stout and tapering pretty regularly to the genicular lobes, about two and three quarters times longer than broad, the middle of the distal half of the inner surface above with a small cluster of raised points, in the female much slenderer and with the apical fourth subequal, the outer carina uniformly elevated, delicately serratulo-spinous through most of its extent (♂), or with a few distant spinules in the outer half (♀), the inner carina armed as the outer but somewhat more delicately (♂) or with a few raised points (♀), the intervening sulcus moderate. Hind tibiæ somewhat longer than the femora, straight in both sexes, armed beneath with a single subapical spine besides the apical pair; spurs subopposite, the basal scarcely beyond the end of the proximal fourth of the tibia, about as long as the tibial depth, set at an angle of about 50° with the tibia and divaricating about 90°, faintly incurved; inner middle calcaria much longer than the outer, nearly twice as long as the others or as the spurs, but much shorter than the first joint of the tarsus. Hind tarsi not much less than half as long as the tibiæ, the first joint almost as long as the rest together, the second twice as long as the third and with it as long as the fourth. Cerci very short and not very slender. Ovipositor about a fifth longer than the fore femora, straight, not stout and delicately tapering in basal half, the tip upturned and very acuminate, the teeth of the inner valves aculeate, straight.

Length of body, ♂ ♀ 11.5 mm.; pronotum, ♂ 4.5 mm., ♀ 4.35 mm.; fore femora, ♂ 4.75 mm., ♀ 4.5 mm.; hind femora, ♂ 10.75 mm., ♀ 13.4 mm.; hind tibiæ, ♂ 11.1 mm., ♀ 14.5 mm.; ovipositor, 5.3 mm.

1 ♂, 1 ♀. Tyrone, Ky., April 23 (S. Garman).

The single ♀ has but one hind leg, and this has been attached after breaking off. As the leg seems to be abnormally different from that of the ♂, it is quite possible that it does not belong to this specimen, and that the characters given above drawn from it should be eliminated.

25. CEUTHOPHILUS FUSIFORMIS, sp. nov.

Body testaceous almost wholly overlaid with black above, the abdomen wholly, the meso- and metanotum all but an anterior mesial spot, and the pronotum to such a degree that the testaceous is confined to a large equilateral triangular patch on each side, the inferior margins for their base and a couple of small mesial patches, the larger behind; the lower half of the sides throughout, however, is pallid testaceous; the legs are testaceous and uniform except for rather faint fuscous scalariform markings on the hind femora. The antennæ are slender and about three times as long as the very compact body, and the legs short and not very slender. Fore femora distinctly stouter than the middle femora, somewhat less than half as long as the hind femora and but little longer than the pronotum, the inner carina armed only with a strong subapical spine. Middle femora armed with 2–3 spines on the front carina, the distal scarcely or no longer than the others, and on the hind carina 2–3 spines besides a moderate genicular spine. Hind femora as long as the body, a little more than twice as long as the fore femora, very stout, the subequal apical portion not over one seventh of the whole, which is three times as long as broad only, a few scattered raised points beyond the middle above, the outer carina uniformly and rather closely serrulate, the inner carina similarly but more delicately armed with a tendency to a biseriate arrangement, the intervening sulcus rather broad. Hind tibiæ straight, shorter than the femora, armed beneath with a single subapical spine besides the apical pair; spurs subopposite, the basal at the end of the proximal fourth of the tibia, nearly half as long again as the tibial depth, set at an angle of about 55° with the tibia and divaricating about 100°, their extreme tips incurved; inner middle calcaria barely longer than the outer, half as long again as the others or as the spurs, and a little shorter than the first tarsal joint. Hind tarsi almost half as long as the tibiæ, the first joint about as long as the rest together, the second fully twice as long as the third and with it as long as the fourth. Cerci moderately slender, considerably shorter than the femoral breadth.

Length of body, 10.5 mm.; antennæ, (est.) 28+ mm.; pronotum, 4.25 mm.; fore femora, 4.75 mm.; hind femora, 10.3 mm.; hind tibiæ, 9.75 mm.

1 ♂. Lincoln, Nebraska, L. Bruner.

26. CEUTHOPHILUS SALLEI, sp. nov.

Dark mahogany brown, glabrous, marked with reddish luteous in a more regular pattern than common, there being a moderately broad mesial stripe of the brighter color, broader on the anterior than the posterior part of the segments, the sides with regularly disposed flecks and dots of luteous, becoming more numerous below, so that the luteous prevails on the lower portion of the sides; on the abdomen the luteous spots are usually either circular or made of short oblique dashes; the legs are as dark as the upper surface, the hind femora with the usual pattern, but the lighter portions subdued in tint. The legs are rather short, the antennæ not stout. Fore femora stouter than the middle femora, especially on the proximal half, about a fifth longer than the pronotum, at least in the ♂, very much less than half as long as the hind femora, the inner carina with a couple of spines, the subapical long. Middle femora with two spines besides a long subapical spine on the front carina, and on the hind carina 0–2 spines besides the long genicular spine. Hind femora fully as long as the body, nearly two and a half times longer than the fore femora, very stout, tapering so that the distal fourth is subequal, nearly three times as long as broad, the inner surface scabrous with a cluster of raised points near the middle above, the outer carina with 8–10 distant unequal serrations or spines, one before the middle of the distal half longer than the others and nearly as long as the tibial spurs, stout at base only (♂) or minutely and distantly denticulate in the distal half (♀), the inner carina with a similar number of small subequal and subequidistant spines (♂), or as in the male (♀), the intervening sulcus narrow and deep. Hind tibiæ slender and straight in both sexes, scarcely longer than the femora, armed beneath with a single preapical spine besides the apical pair; spurs generally opposite, the basal at about the end of the proximal third of the tibia, fully half as long again as the tibial depth, set at an angle of about 50° with the tibia and divaricating about 140° with each other, their tips incurved; inner middle calcaria very much longer than the outer, more than twice as long as the others or as the spurs and fully as long as the first tarsal joint. Hind tarsi almost half as long as the tibiæ, the first joint nearly as long as the rest together, the second more than twice the length of the third and with it not so long as the fourth. Cerci tapering throughout equally, a little shorter than the femoral breadth, the tip not very pointed. Ovipositor tapering gently in proximal, equal in distal half, the tip upcurved and produced to a fine point, as long as the fore femora, the teeth and apical hook of inner valves slender, long, and arcuate.

Length of body, ♂ 16 mm.. ♀ 14.5 mm.; pronotum, ♂ 5.7 mm., ♀ 5.5 mm.; fore femora, ♂ 6.9 mm., ♀ 6 mm.; hind femora, ♂ 17.5 mm., ♀ 14.8 mm.; hind tibiæ, ♂ 18 mm., ♀ 15 mm.; ovipositor, 6 mm.

1 ♂, 7 ♀. New Orleans, Auguste Sallé.

The species is noticeable for the length of all the spines.

27. CEUTHOPHILUS LATENS.

Ceuthophilus latens Scudd., Bost. Journ. Nat. Hist., vii. 437 (1862); Walk., Catal. Derm. Salt. Brit. Mus., i. 202 (1869); Brun., Publ. Nebr. Acad. Sc., iii. 31 (1893); Blatchl.!, Proc. Ind. Acad. Sc., 1892, 143–144 (1894).

Body glabrous, with a broad mediodorsal stripe of dark rufo-luteous on the thoracic segments, bordered very broadly on either side with blackish or blackish fuscous, fading out inferiorly, the lower portion of the sides pallid luteous, more or less impure, the very margin luteo-testaceous; the abdominal segments obscurely continue these longitudinal markings, but the black becomes brownish fuscous and is so dotted with dull luteous as to give a very different appearance, the segments being marked with alternate and frequent short longitudinal or obliquely longitudinal bars of brownish fuscous and dull luteous, the darker parts often also dotted with luteous; legs luteous, more or less infuscated, especially the hind femora the outer surface of which excepting at base is increasingly fuscous distally and broadly annulate with blackish apically, the surface generally sprinkled with luteous dots, with faintly different depths of color marking a scalariform pattern. The hind tibial spines are distinctly blackish at the base. The antennæ are about three times as long as the body, luteous, the joints at first feebly infuscated at the base, afterwards wholly, and then interrupted by luteous for a single joint every few joints irregularly, the legs moderately slender and not very long, the hind tibial spurs distinctly infuscated or blackish at base. Fore femora slightly stouter than the middle femora, considerably less than half as long as the hind femora, nearly a third longer than the pronotum in the ♂, though but little longer in the ♀, the inner carina armed with 2–3 spines. Middle femora with generally 2–3 spines on the front carina and on the hind carina 1–2 spines besides a moderate genicular spine. Hind femora about as long as the body, at least two and a quarter times longer than the fore femora, the swollen portion very gradually tapering and of unusual length, the whole about three and a quarter (♂) or three and three quarters (♀) times as long as broad, the surface with no raised points, both outer and inner carina in both sexes almost unarmed, at most a few feeble spinules being seen near the apex, the intervening sulcus narrow. Hind tibiæ scarcely or no longer than the femora, straight in both sexes, slender, generally armed beneath with two median subapical spines besides the apical pair; spurs irregularly opposite, the basal at the end of the proximal third of the tibia, slightly longer than the tibial depth, set at an angle of about 45° with the tibia and divaricating about 120°, slightly incurved especially at tip; inner middle calcaria much longer than the outer, more than twice as long as the others or as the spurs, and as long as the first tarsal joint. Hind tarsi about two fifths as long as the hind tibiæ, the first joint as long as the rest together, the second more than twice as long as the third and with it as long as the fourth. Cerci rather slender, tapering, pointed, about two thirds as long as the femoral breadth. Ovipositor twice as long as the fore femora, and about two thirds as long as the hind femora. straight. gently tapering in the proximal, rather slender and equal in the distal half, the tip upturned and acute but not aculeate, the armature of the inner valves consisting of deep denticulations.

Length of body, ♂ 14.5 mm., ♀ 16 mm.; antennæ, ♀ (est.) 44 mm.;

pronotum, ♂ 4.6 mm., ♀ 5 mm.; fore femora, ♂ 6 mm., ♀ 5.5 mm.; hind femora, ♂ ♀ 14 mm.; hind tibiæ, ♂ 14.5 mm., ♀ 14 mm.; ovipositor, 9 mm.

7 ♂, 6 ♀. Ithaca and Endfield Falls, N. Y. (Cornell Univ., Morse); Vigo Co., Ind. (Blatchley); Texas, Belfrage. Originally described from Illinois. Said by Bruner to be found in Eastern Nebraska, but I have seen no specimens from so far west.

28. CEUTHOPHILUS MERIDIONALIS, sp. nov.

Whole dorsal surface of body dark, being mostly almost piceous with dark mahogany brown markings consisting principally of a broad mesial stripe of irregular width on the thorax, fully as broad as the basal joint of the antennæ and on the abdomen made up of numerous spots and short longitudinal or oblique bars, which toward the sides become tinged with luteous; the sides dingy luteous, the femora fusco-luteous, the hind pair externally striped with clearer luteous above and spotted below; hind femoral geniculations blackish; all the tibiæ and antennæ dark luteous. The antennæ are moderately slender, the legs rather long. Fore femora scarcely stouter than the middle femora, fully one fourth longer than the pronotum but only two fifths the length of the hind femora, the inner carina with two spines, the outer of which is hardly subapical but pretty stout. Middle femora with three pretty stout spines on the front carina, and on the hind carina from 1–4 small spines besides a long genicular spine. Hind femora of the length of the body, about two and a half times as long as the fore femora, very stout, the apical fourth subequal, about three and a quarter times as long as broad; the upper half very faintly but closely scabrous in the darker portions, the outer carina elevated, with 5–6 unequal and inequidistant large or very large spines, the largest just beyond the middle, coarse, especially at base, and much longer than the tibial spurs, besides one or two spinules in the constricted portion of the femora, the inner carina rather distantly and rather regularly spinulate throughout, the intervening sulcus very broad. Hind tibiæ gently arcuate on basal third, much longer than the femora, not very slender, armed beneath apically with two or three spines besides the apical pair; spurs subalternate, the basal at end of proximal third of the tibia, slightly longer than the tibial depth, set at an angle of 45° with the tibia and divaricating about 100°, the apical half incurved; (calcaria and hind tarsi lost in the only specimen known). Cerci slender, gently tapering, about two thirds as long as the femoral breadth.

Length of body, 20 mm.; antennæ, 25× mm.; pronotum, 6.5 mm.; fore femora, 8.25 mm.; hind femora, 20.5 mm.; hind tibiæ, 22.3 mm.

1 ♂. Chihuahua, Mexico.

29. CEUTHOPHILUS NEGLECTUS, sp. nov.

Ceuthophilus maculatus (pars), Scudd.!, Bost. Journ. Nat. Hist., vii. 434 (1862).

Glabrous, castaneous, more or less, often deeply, infuscated especially above, the infuscation often but not always terminating below the middle of the sides, which are there sordid luteous; a broad more or less and often very obscure mediodorsal rufo-luteous stripe on the pronotum, sometimes extended farther back but then generally broken; the sides of the pronotum and to a lesser extent the meso- and metanotum are more or less blotched or vermiculate with luteous, and the abdomen is more or less but generally feebly maculate with luteous; the markings and the coloring vary greatly, so that it is difficult to formulate any general statement; the female is apt to be darker than the male, and specimens from New England are often almost uniformly dark, even almost black, while the contrasts between the dorsum and the lower portion of the sides are strongest in specimens from the Middle Atlantic States, where they grow to a large size; the legs are generally luteo-castaneous, the tips of all the femora dark, sometimes almost black, the hind femora with scalariform fuscous markings. The antennæ are not often infuscated and then generally more or less or feebly annulate with luteous, slender and generally 2–3 times as long as the body, the legs rather slender and moderately short. Fore femora scarcely stouter than the middle femora, considerably less than half as long as the hind femora and but very little longer than the pronotum, the inner carina with a subapical spine, rarely accompanied by another. Middle femora with 1–3 spines (largely depending upon age) on the front carina, and on the hind carina 0–3 spines besides a longer but short genicular spine. Hind femora two and a quarter times longer than the fore femora, about as long as the body, stout and tumid, the upper and lower margins almost equally arcuate, scarcely more than the genicular portion subequal, almost three times as long as broad, the inner surface with a very few raised points next or at the upper margin beyond the middle, scarcely perceptible or absent from the female, the outer carina minutely, closely, and pretty uniformly serrulate through all but the basal third, sometimes almost imperceptible in the female, the inner carina a feebler repetition of the outer, the intervening sulcus moderate in width. Hind tibiæ slender, straight in both sexes, barely or no longer than the femora, armed beneath with 1–2 subapical spines besides the apical pair; spurs subopposite, the basal at the end of the proximal third of the tibia, scarcely shorter than the tibial depth, set at an angle of about 45° with the tibia and divaricating about 100–110°, their tips incurved: inner middle calcaria considerably longer than the outer, about twice as long as the others or as the spurs, but shorter than the first tarsal joint. Hind tarsi almost two fifths as long as the tibiæ, the first joint not so long as the rest together, the second considerably more than twice as long as the third and with it fully as long as the fourth. Cerci moderately stout, tapering rather uniformly, about two thirds as long as the femoral breadth. Ovipositor half as long as the hind tibiæ, straight, tapering in basal half, equal and moderately slender, the tip slightly upcurved and acutely pointed (about 35°), the inner valves with aculeate, scarcely arcuate teeth.

Length of body, ♂ ♀ 12.5 mm.; pronotum, ♂ 4.4 mm., ♀ 4.6 mm.; fore femora, ♂ ♀ 5 mm.; hind femora, ♂ 12 mm., ♀ 11.7 mm.; hind tibiæ, ♂ ♀ 12 mm.; ovipositor, 6 mm.

31 ♂, 29 ♀. Ithaca, N. Y., Comstock (Cornell Univ., Morse); Jay, Vt. (A. P. Morse); Sudbury, Vt. (S. H. Scudder); side of Mt. Washington, N. H. (S. H. Scudder); Forest Hills, Mass. (S. Henshaw); Cambridge, Mass. (Mus. Comp. Zoöl.); Princeton, Mass. (S. H. Scudder); Pennsylvania (Mus. Comp. Zoöl.); Maryland (P. R. Uhler); Baltimore, Md. (Mus. Comp. Zoöl.); Washington, D. C. Cornell Univ., L. Bruner); Virginia (L. Bruner); West Virginia (Museum Comp. Zoöl.). In the U. S. National Museum, from C. V. Riley's collection, are 3 ♂, 2 ♀, from Maryland, District of Columbia, and Virginia.

30. CEUTHOPHILUS MACULATUS.

Rhaphidophora maculata [Say, MS.], Harr., Treat. Ins. Inj. Veg., ed. 1841–42, 126; Fitch, Amer. Journ. Agric. Sc., vi. 146 (1847); Pack., Rep. Nat. Hist. Me., 1861, 375; Thom., Trans. Ill. St. Agric. Soc., v. 444 (1865).

Phalangopsis maculata Harr., Treat. Ins. Inj. Veg., ed. 1852, 137; ed. 1862, fig. 73; Walk., Cat. Derm. Salt. Brit. Mus., i. 116 (1869).

Ceuthophilus maculatus Scudd.! (pars), Bost. Journ. Nat. Hist., vii. 434 (1862); Pack., Rep. Nat. Hist. Me., 1862, 196; Smith, Proc. Portl. Soc. Nat. Hist., i. 145 (1868); Pack., Guide Ins., 565 (1869); Walk., Cat. Derm. Salt. Brit. Mus., i. 201 (1869); Id., Ibid., Suppl., v. 23 (1871); Smith, Rep. Conn. Bd. Agric., 1872, 359, 380;

Glov., Ill. N. A. Ent., Orth., pl. 3, fig. 5 (1872); Scudd., Hitchc., Rep. Geol. N. H., i. 366 (1874); Prov., Nat. Canad., viii. 75, fig. 5 (1876); Putn., Proc. Dav. Acad. Sc., ii. 11 (1876); Bol., Ann. Soc. Ent. France (5), x. 72 (1880); Ril., Stand. Nat. Hist., ii. 184, fig. 259 (1884); Brun.?, Bull. Washb. Coll. i. 126 (1885); Caulf., Can. Ent., xviii. 212 (1886): Id., Rep. Ent. Soc. Ont., xviii. 63, 69 (1888); Brunn., Monogr. Stenop., 63 (1888); Pack., Mem. Nat. Acad. Sc., iv. 72, 116 (1888); Fern., Orth. New Engl., 19 (1888); Pack., Psyche, v. 198 (1889); Davis, Ent. Amer., v. 80 (1889); Smith, Cat. Ins. N. Jers., 409 (1890); Charlt.?, Ent. News, i. 64 (1890); Cock.?, Can. Ent., xxii. 76 (1890); McNeill, Psyche, vi. 27 (1891); Osb., Proc. Iowa Acad. Sc., i. ii. 119 (1892); Towns.?, Ins. Life, vi. 58 (1893); Blatchl., Proc. Ind. Acad. Sc., 1892, 142–143 (1894); Cock.?, Trans. Amer. Ent. Soc., xx. 336 (1894).

Phalangopsis lapidicola Uhl, Harr. Treat. Ins. Inj. Veg., 155 (1862).

Ceuthophilus lapidicolus Brun.!, Publ. Nebr. Acad. Sc., iii. 32 (1893).

Color and markings almost precisely the same as in *C. terrestris*, so that imperfect and immature specimens are exceedingly difficult to separate; but the darker markings in this species are as a rule darker and cover the surface to a greater extent, and when the mediodorsal stripe is present it is often broader and extends upon the meso- and metanotum; on the other hand, the maculation of the abdomen with luteous is usually more striking in the present species (partly from the darkness of the ground) and forms sometimes a tolerably regular pattern, consisting on each joint of an anterior mediodorsal triangular spot, a central subdorsal oblique dash, and posterior spots farther from the middle line. The antennæ are from two to three times as long as the body, and slender except at extreme base, and the legs are moderately long. Fore femora no stouter than the middle femora, a little more than a fourth longer than the pronotum and much less than half as long as the hind femora, the inner carina with a long subapical spine and occasionally an additional one. Middle femora with 0–2 spines besides a rather long subapical spine on the front carina, and on the hind carina an occasional small spine besides a long genicular spine. Hind femora of about the length of the body, three and a half times as long as broad, about two and a third times as long as the fore femora; moderately stout at base, the distal fifth subequal, with no raised points on the upper or inner surface, the outer carina with about thirteen unequal coarse spines, the longest hardly half as long as the tibial spurs (♂) or with minute distant inconspicuous spinules (♀), the inner carina with similar but uniform spinulation, none so large as on the outer carina (♂) or with a few minute spinules on the apical half (♀), the intervening sulcus not very broad. Hind tibiæ feebly undulate in the basal half in the male, slender in both sexes, distinctly but not greatly longer than the femora, armed beneath with a single preapical spine or occasionally with two minute unaligned spines besides the apical pair; spurs rudely opposite, the basal at the end of the proximal third of the tibia, more than half as long again as the tibial depth, set at an angle of about 40° with the tibia and divaricating 90–100°, their tips incurved; inner and outer middle calcaria subequal, more than twice as long as the others or as the spurs, and as long as the first tarsal joint. Hind tarsi about two fifths as long as the tibiæ, the first joint shorter than the rest together, the second twice as long as the third and with it longer than the fourth. Cerci stout in the proximal half, tapering beyond, about two thirds as long as the femoral breadth. Ovipositor nearly two thirds as long as the hind femora, shaped and armed as in *C. terrestris.*

Length of body, ♂ 14 mm., ♀ 16? mm.; pronotum, ♂ 5 mm., ♀ 5.1 mm.; fore femora, ♂ 6.6 mm., ♀ 6.7 mm.; hind femora, ♂ 15.25 mm., ♀ 16 mm.; hind tibiæ, ♂ 16.25 mm., ♀ 17 mm.; ovipositor, 10 mm.

18 ♂, 9 ♀. Montreal, Canada, Caulfield; valleys of the White Mts., N. H.; Chateaugay Lake, Adirondacks, N. Y., 2,000′, F. C. Bowditch; Ithaca, N. Y., Pearce, Pettit (Corn. Univ.); Michigan, J. G. Jack; Cape Elizabeth, Me., E. S. Morse; Blue Hills, Milton, Mass., S. Henshaw; Mass., F. G. Sanborn; Conn., E. Norton; New York; S. Orange, N. J.; Moline, Ill., McNeill; Vigo Co., Ind., W. S. Blatchley; Iowa City, Iowa, Shimek (Bruner). I have also seen specimens in the Museum of Comparative Zoölogy from Norway (Smith), Gorham, Cape Elizabeth (Morse), Maine, Vermont, Malden (Higgins), House Island (Cooke), Feltonville (Jilson) and Nahant, Mass. In addition to the districts mentioned above it has been reported (but may often have been erroneously taken for another species) from Howe's Cave, N. Y. (Packard), Missouri (Brunner), McPherson Co., Kansas and Nebraska (Bruner), and Colorado (Charlton, Cockerell, Townsend).

31. CEUTHOPHILUS TENEBRARUM, sp. nov.

Ceuthophilus latens McNeill!, Psyche, vi. 27 (1891).

Body glabrous, brownish or blackish fuscous, heavily marked with luteo-castaneous, often more or less pallid, sometimes with a rufous tinge; the markings consist of a mediodorsal stripe of varying width but usually rather broad on the pronotum, especially a little before either border, generally reduced to a line on the abdomen, a large lateral patch on either side of the pronotum, sometimes confined to the inferior margin, sometimes extending half way to the mediodorsal line, and a conspicuous and liberal sprinkling of roundish spots, generally more or less elongated longitudinally, especially on the abdomen; the antennæ are pale fuscous and the legs sordid luteous more or less infuscated, the hind femora with heavy fuscous scalariform markings, leaving roundish dull luteous spots in the openings of the upper half. The antennæ are slender and apparently only about twice the length of the body or a little more, and the legs short though slender. Fore femora of the same slenderness as the middle femora, much less than half as long as the hind femora and a little more (♂) or a little less (♀) than a fourth longer than the pronotum, the inner carina with 1–2 small spines. Middle femora with 1–3 spines on the front carina, the subapical the longest but not long, the hind carina with rarely more than the moderately short genicular spine. Hind femora somewhat shorter than the body, about two and a half times longer than the fore femora, moderately slender, being about three and a third times as long as broad, fully the apical fourth subequal, the surface with no raised spines, the outer carina with a few distant serrations or recumbent spines on apical half (♂) or unarmed (♀), the inner carina similar to the outer, the intervening sulcus narrow. Hind tibiæ straight in both sexes, not a great deal longer than the femora, armed beneath with a single subapical spine besides the apical pair; spurs subalternate, the basal at the end of the proximal third of the tibia, scarcely if any longer than the tibial depth, set at an angle of 45° with the tibia and divaricating about 110°, their tips incurved; inner middle calcaria much longer than the outer, more than twice as long as the others or as the spurs, and nearly as long as the first joint of the tarsus. Hind tarsi fully two fifths as long as the tibiæ, the first joint almost as long as the rest together, the second twice as long as the third and with it fully as long as the fourth. Cerci slender, tapering regularly, three fourths as long as the femoral breadth. Ovipositor as long as the fore femora, straight, the apical three fifths equal and moderately slender, the apex a little upturned and subacute but not very much produced, the teeth of the inner valves consisting of blunt pointed crenations.

Length of body, ♂ 13.5 mm., ♀ 12.5 mm.; pronotum, ♂ 3.75 mm., ♀ 3.8 mm., fore femora, ♂ 4.8 mm., ♀ 4.25 mm.; hind femora,

♂ 11.75 mm., ♀ 10.25 mm.; hind tibiæ, ♂ 12.5 mm., ♀ 10.6 mm.: ovipositor, 4.25 mm.

7 ♂, 4 ♀. Port Byon, Ill., July 7 (McNeill); S. Illinois (Kennicott); Lexington, Ky., May, June, August (S. Garman); Bee Spring, Ky., June, Sanborn (Mus. Comp. Zoöl.); Beaufort, N. C., Shute (Mus. Comp. Zoöl.). 2 ♂, 2 ♀, from Ohio are in the collection of Riley (U. S. Nat. Mus.).

32. Ceuthophilus bicolor, sp. nov.

Body glabrous, luteo-testaceous, with a broad subdorsal blackish fuscous band on either side, leaving between them a broad bright stripe the whole length of the body, next the stripe sharply delimited, laterally more or less broken, ragged and fading away, narrow on the pronotum where it is infringed upon by a large central luteous spot on the sides, broader and profusely spotted with luteous posteriorly, the lower portions of the sides almost wholly pallid luteous with cloudy infuscations, the extreme margin testaceous; legs luteo-testaceous, the hind femora feebly marked with fuscous in a scalariform pattern and tipped with fuscous. The *antennæ* are slender and at least three times as long as the body, and the legs slender and rather short. Fore femora no stouter than the middle pair, much less than half as long as the hind femora, a fifth as long again as the pronotum, the inner carina with two or three spines, the preapical much longer than the others. Middle femora with the front carina similarly armed and the hind carina with one or two spines mesially situated besides a long genicular spine. Hind femora as long as the body, two and a half times longer than the fore femora, stout, tapering with great regularity to the slightly enlarged genicular lobes, scarcely more than three times as long as broad, the inner surface above beyond the middle with a small cluster of raised points, the outer carina armed on the stouter part of the femora with an open series of serrulations, developing distally into spines, the last two much larger than the others and half as long as the tibial spurs, followed by 3–4 slight spines just before and on the genicular lobes, the inner carina equally but inequidistantly and rather sparsely spinulate, the intervening sulcus broad. Hind tibiæ straight, slender, more than a tenth longer than the femora, armed beneath with a single subapical spine besides the apical pair; spurs subalternate, the basal before the end of the proximal third of the tibia, nearly or quite twice as long as the tibial depth, set at an angle of about 50° with the tibia and divaricating about 110°, their tips incurved; inner middle calcaria greatly longer than the outer, more than twice as long as the others or as the spurs, and fully as long as the first tarsal joint. Hind tarsi barely two fifths as long as the tibiæ, the first joint as long as the rest together, the second three times as long as the third and with it as long as the fourth. Cerci not very slender, blunt tipped, about two thirds as long as the femoral breadth.

Length of body, 11.5 mm.; antennæ, (est.) 32+ mm.; pronotum, 3.75 mm.; fore femora, 4.5 mm.; hind femora, 11.5 mm.; hind tibiæ, 13 mm.

1 ♂. Bee Spring, Ky., June 14, F. G. Sanborn (Mus. Comp. Zoöl.).

33. CEUTHOPHILUS NODULOSUS.

Ceuthophilus nodulosus Brunn., Monogr. Stenop., 64, fig. 33a (1888).

Luteo-castaneous, heavily marked with blackish fuscous especially along the posterior borders of all the segments and the anterior border of the pronotum, and the latter also flecked with it in an obscure fashion upon the whole disk; legs luteous, the hind femora almost lacking the usual scalariform markings. The antennæ are slender, but are apparently less than twice the length of the body, the legs short. Fore femora very slightly stouter than the middle femora, slightly (♂) or no (♀) longer than the pronotum and distinctly less than half as long as the hind femora, the inner carina with a feeble subapical spine, at least in the male. Middle femora generally with 3–4 small spines on the front carina, and on the hind carina 0–1 (♀) or 3–8 (♂) short spines besides a short genicular spine. Hind femora pretty stout, a very brief apical portion equal, a little less than three times as long as broad, considerably more than twice as long as the fore femora, all the scalariform dark portions of the surface, especially in the male, scabrous with raised points, which are also clustered about the upper portion of the inner side just beyond the middle, the outer carina elevated, with three or four inequal and irregularly distant large and rather coarse more or less arcuate spines, the longest nearly or quite as long as the tibial depth, placed in the middle half, besides a few minor spines beyond them (♂) or with 4–5 small distant spines, most of them in the constricted part of the femora (♀), the inner carina with a series of closer but in no way crowded smaller and uniform spinules, subobsolete in the female, the intervening sulcus moderate in breadth. Hind tibiæ strongly bent or bowed near the middle and subsinuate, on the middle of the proximal half compressed to form a triangular denticle on the under surface, from which a regular curve sweeps to an inferior slight spiniferous swelling just before the middle of the distal half (♂), shorter than the femora in both sexes, armed beneath on the distal half with a series of about three recumbent spines (in the ♂ arising from slight elevations) besides the apical pair; spurs subopposite, the basal well beyond the end of the distal third of the tibia, hardly more than half as long as the tibial depth, set at an angle of about 45° with the tibia and divaricating about as much; inner middle calcaria somewhat longer than the outer, twice as long as the others or as the spurs but much shorter than the first tarsal joint. Hind tarsi less than two fifths the length of the tibiæ, the first joint nearly as long as the rest together, the second fully twice as long as the third and with it as long as the fourth. Cerci very short, not very slender, rapidly tapering, hardly more than half as long as the femoral breadth (♀) or developed basally as a single stout subclavate apically upturned blunt joint, surmounted by a brief conical multiarticulate appendage, the only portion which surpasses the supra-anal plate (♂). Ovipositor brief and slight, no longer than the fore femora, tapering in proximal, equal in distal half, the apex and armature as in *C. inquinatus.*

Length of body, ♂ 13.5 mm., ♀ 12 mm.; pronotum, ♂ 4 mm., ♀ 3.8 mm.; fore femora, ♂ 4.5 mm., ♀ 3.6 mm.; hind femora, ♂ 10.5 mm., ♀ 8.5 mm.; hind tibiæ, ♂ 9.6 mm., ♀ 8 mm.; ovipositor, 3.5 mm.

2 ♂, 2 ♀. West Point, Nebr.; McPherson Co., Kans., Rundstrom, all from L. Bruner. Subsequently to the description of the above I received from the U. S. National Museum 3 ♂, 1 ♀, from Dallas, Texas, of considerably larger size, like that described by Brunner, also from Texas.

34. Ceuthophilus valgus, sp. nov.

Dark luteo-testaceous, more or less infuscated especially along the hind borders of all the segments and the front border of the pronotum; occasionally a few indistinct luteous dots occur in a transverse series on the abdominal segments, but most of the varied markings are confined to the pronotum, where they are not pronounced and consist of a dull luteous mediodorsal stripe and vague and irregular streaks or clouds of luteous upon either side, more or less extensive; the legs are generally lighter than the body, but are more or less infuscated beyond the base of the femora, the hind pair of which scarcely show any scalariform markings. The antennæ are not very slender, two to three times as long as the body, and the legs are moderately long and slender. Fore femora no stouter than the middle femora, less than a quarter longer than the pronotum and somewhat less than half as long as the hind femora, the inner carina with a single minute spine, at least in the ♂, besides a distinct preapical spine. Middle femora with a single spine (♀) or 2–4 spines (♂) on the front carina, and on the hind carina about four spines (generally fewer in the ♀) besides a short genicular spine. Hind femora nearly as long as the body, distinctly more than twice as long as the fore femora, not very stout, being about three and a quarter times longer than broad, glabrous, the surface with no raised points, the outer carina elevated, armed with about ten unequal and inequally separated spines, the largest stouter than and about as long as the tibial spurs (♂) or scarcely elevated and unarmed (♀), the inner carina with distant raised thick points, occasionally becoming minute spines (♂) or unarmed (♀), the intervening sulcus narrow. Hind tibiæ as long as the femora, straight in the ♀, strongly bowed on proximal half in the ♂ (unless immature), armed beneath with a single preapical spine besides the apical pair; spurs subopposite, the basal at about the end of the proximal third of the tibia, scarcely if at all longer than the tibial depth, set at an angle of about 50° with the tibia and divaricating about 100°, their tips incurved; inner middle calcaria about a third longer than the outer, twice as long as the others or as the spurs, but hardly more than half as long as the first tarsal joint. Hind tarsi less than half as long as the tibiæ, the first joint nearly as long as the rest together, the second more than twice as long as the third and with it fully as long as the fourth. Cerci stout, tapering, pointed, hardly more than half as long as the femoral breadth. Ovipositor almost as long as the hind tibiæ, rather slender, equal from close to the base to near the tip, gently arcuate, the tip barely upturned and pointed at an angle of not less than 50°, the inner valves scarcely armed, the teeth being barely indicated by a slight crenulation.

Length of body, ♂ 13 mm., ♀ 10 mm.; pronotum, ♂ 4.7 mm., ♀ 3.65 mm.; fore femora, ♂ 5.5 mm., ♀ 4.5 mm.; hind femora and tibiæ, each, ♂ 12.9 mm., ♀ 9.4 mm.; ovipositor, 8.5 mm.

6 ♂, 3 ♀. Colorado 7–8,000′, H. K. Morrison; South Park, Colorado, 8–10,000′, August 11–16, S. H. Scudder. I also place here an immature ♀ taken by me at Pueblo, Colorado, 4,700′, August 30–31. Since the description was written, Mr. L. Bruner has sent me 1 ♂, 2 ♀, from Brush Creek, Custer Co., Colorado, 10,000′, and Granite, Colorado.

35. CEUTHOPHILUS DIVERGENS.

Ceuthophilus divergens Scudd.!, Bost. Journ. Nat. Hist., vii. 436 (1862); Walk., Cat. Derm. Salt. Brit. Mus., i. 201 (1869); Thom.?, Proc. Acad. Nat. Sc. Philad., 1870, 77; Id.?, Ann. Rep. U. S. Geol. Geogr. Surv. Terr., ii. 265, 269 (1871); Id.?, Bull. U. S. Geol. Geogr. Surv. Terr., iv. 485 (1878); Ril., Stand. Nat. Hist., ii. 184 (1884); Blatchl., Proc. Ind. Acad. Sc., 1892, 153 (1894).

Body subglabrous, dark blackish fuscous above, passing on the sides into rufo-testaceous more or less tinged with luteous, and with blotches and irregular spots of the same above; especially to be noted are a mediodorsal rufo-luteous interrupted stripe and on the sides of the pronotum a large spot of the same much vermiculate with fuscous; the abdomen is also more or less spotted with the same; the legs are dingy luteous, all the femora tipped with fuscous and the hind femora heavily marked with fuscous in a scalariform pattern. The antennæ are moderately slender and three or four times as long as the body, and the legs are rather long and slender, with prominent spines. Fore femora no stouter, but in the male slightly shorter, than the middle femora, much less than half as long as the hind femora and but little longer than the pronotum, the inner carina with 2–3 spines, the subapical long. Middle femora with 2–3 spines on the front carina, the subapical longest, and on the hind carina two small spines besides a long genicular spine. Hind femora about as long as the body, about two and a half times longer than the fore femora, moderately stout particularly in the male, where they are less than three and a half times while in the female they are nearly four times as long as broad, the middle of the inner surface in the male with a considerable cluster of raised points on the upper half, the outer carina with about ten unequal stout teeth the largest shorter but stouter than the tibial spurs (♂) or apically with a series of subdued serrulations (♀), the inner carina in ♀ armed like the outer carina but very inconspicuously, in the ♂ as in the ♀ but more conspicuously, the intervening carina narrow. Hind tibiæ scarcely longer than the femora, straight in both sexes, slender, distinctly though feebly constricted at the base, faintly enlarging above toward the apex, armed beneath with a single subapical spine besides the apical pair; spurs subalternate, the basal at the end of the proximal fourth of the tibia, nearly or quite twice as long as the tibial depth, set at an angle of about 70° with the tibia and divaricating from 130° to 180°, their tips incurved; inner middle calcaria much longer than the outer, fully twice as long as the others or as the spurs, and as long as the first tarsal joint in the ♂, scarcely so long in the ♀. Hind tarsi less than half as long as the hind tibiæ, the first joint almost equalling the rest together, the second much more than twice as long as the third and with it about as long as the fourth. Cerci rather stout and short, hardly exceeding in length half the femoral breadth. Ovipositor nearly straight and short, shorter than the fore femora, the basal half tapering, the apical half slender and equal, the tip more than usually upturned and produced to a very acuminate point, the teeth of the inner valves long, aculeate, arcuate.

Length of body, ♂ 12 mm., ♀ 13 mm.; antennæ, (est.) ♂ 40 mm., ♀ 48 mm.; pronotum, ♂ 4.5 mm., ♀ 5 mm.; fore femora, ♂ 5.4 mm., ♀ 5.25 mm.; hind femora, ♂ 13.5 mm., ♀ 12.75 mm.; hind tibiæ, ♂ 13.75 mm., ♀ 13 mm.; ovipositor, 4.75 mm.

1 ♂, 2 ♀. Nebraska, A. Agassiz (Mus. Comp. Zoöl.). Thomas reports it from several localities in Colorado, Wyoming, Dakota, and Montana, but it is quite as likely as not that some other species was mistaken for it. The one reported by Osborn and Bruner from Iowa and Nebraska is the one here described as *C. bruneri.*

36. CEUTHOPHILUS OCCULTUS, sp. nov.

Body castaneous, more or less and irregularly blotched above with feeble fuscous markings, most conspicuous on the pronotum and absent from a narrow irregular and sometimes broken median stripe of the ground color, which does not extend upon the abdomen; abdomen obscured with fuscous on the posterior margins of the segments. Legs luteo-castaneous, the outside of the hind femora with the usual markings nearly obsolete. Antennæ very long and slender, the legs moderately long. Fore femora a little stouter than the middle femora, about a sixth longer than the pronotum, and half or less than half as long as the hind femora, the inner carina armed with a long preapical spine and sometimes with another short one. Middle femora with a long preapical spine on the front carina, sometimes accompanied in the ♀ by 1–2 others, the hind carina with a long genicular spine accompanied by 2–3 spines in the ♂. Hind femora of about the length of the body in the ♂, about twice (♀) or distinctly more than twice (♂) as long as the fore femora, rather slender, being nearly four times as long as broad, without conspicuous raised points on the surface, the outer carina elevated, with 5–6 distant spinules, the largest very small (♂) or not elevated, with many minute serrulations on the apical half (♀), the inner carina with numerous delicate spinules (♂) or similar to the other carina (♀). Hind tibiæ straight, distinctly longer than the femora, beneath with a single preapical spine besides the apical pair; spurs subopposite, the basal before the end of the proximal fourth of the tibiæ, long and delicate, being nearly twice as long as the tibial depth, set at an angle of about 45° with each other and divaricating about 110°, their tips incurved. Inner middle calcaria a little longer than the outer, twice as long as the others and nearly twice as long as the spurs, as long as the first tarsal joint. Hind tarsi two fifths as long as the tibiæ, the first joint as long as the others together, the fourth about equalling the second and third together. Cerci pretty stout at base, tapering throughout, pointed, longer than the femoral breadth. Ovipositor nearly two thirds as long as the hind femora, pretty stout at base, the distal two thirds equal and rather slender, the apex produced to a fine spinous point and the teeth of the inner valves prominent and sharp, the proximal subdenticulate, the others acicular and arcuate.

Length of body, ♂ 11 mm., ♀ 12 mm.; antennæ, (est.) ♂ 30 mm., ♀ 25 mm.; pronotum, ♂ 4 mm., ♀ 3.75 mm.; fore femora, ♂ 4.7 mm., ♀ 4.5 mm.; hind femora, ♂ 10.5 mm., ♀ 8.5 mm.; hind tibiæ, ♂ 11.5 mm., ♀ 9 mm.; ovipositor, 5.25 mm.

1 ♂, 2 ♀. Georgia, Morrison.

37. CEUTHOPHILUS ALPINUS, sp. nov.

Luteo-testaceous, traversed by distinct and rather broad fuscous bands at the incisures of all the segments (about equally on the anterior and posterior margins) which fade out more or less on the lower portion of the sides; pronotum with two broad subdorsal longitudinal fuscous bars, extending across at least the anterior half of the segment, leaving between them a slender mediodorsal luteous stripe; legs luteo-testaceous, scarcely at all infuscated excepting on the hind femora which sometimes show coarse and obscure scalariform markings. The antennæ are moderately slender and probably do not twice exceed the length of the body, and the legs are short. Fore femora scarcely if at all stouter than the middle femora, but very little longer than the pronotum, about half as long as the hind femora, the inner carina with a subapical spine only. Middle femora armed with 1–2 (♀) or 3–4 (♂) spinules on the front carina, and on the hind carina with 1–2 spinules besides a short genicular spine. Hind femora very much shorter than the body, twice as long as the fore femora, moderately stout, being scarcely more than three times as long as broad, and the enlarged portion long, the surface with exceedingly few scattered raised points on the upper half beyond the middle, the outer carina uniformly and rather finely serrulate, more finely in the ♀ than in the ♂, the inner carina with similar but finer and less frequent serrulations or spinules, the intervening sulcus narrow. Hind tibiæ as long as the femora, straight in both sexes, armed beneath with two distant median spines besides the apical pair; spurs opposite for the most part, the basal at the end of the proximal third of the tibia, no longer than the tibial depth, set at an angle of 45° to the tibia, and divaricating about 60°, their tips incurved; inner middle calcaria of about the same length as the outer, less than twice as long as the others or as the spurs, and fully two thirds as long as the first tarsal joint. Hind tarsi almost half as long as the tibiæ, the first joint distinctly shorter than the rest together, the second twice as long as the third, and with it as long as the fourth. Cerci stout on the basal half, tapering beyond, shorter than the femoral breadth. Ovipositor stout at extreme base, suddenly narrowing to a slender almost straight blade, nearly two thirds as long as the hind tibiæ, the teeth of the inner blades aculeate, arcuate, and long.

Length of body, ♂ 13 mm., ♀ 12.5 mm.; pronotum, ♂ 3.9 mm., ♀ 3.4 mm.; fore femora, ♂ 4.4 mm., ♀ 3.8 mm.; hind femora and tibiæ, each, ♂ 9 mm., ♀ 7.6 mm.; ovipositor, 4.85 mm.

2 ♂, 2 ♀. South Park, Colorado, 8–10,000′, Aug. 11–16, S. H. Scudder; Mt. Lincoln, Colorado, 11–13,000′, above timber, Aug. 13, S. H. Scudder.

38. CEUTHOPHILUS BRUNERI, sp. nov.

Ceuthophilus divergens Osb., Proc. Iowa Acad. Sc., i., ii. 119 (1892); Brun.! (pars), Publ. Nebr. Acad. Sc., iii. 32 (1893).

Obscure brownish fuscous, with luteous markings which are very dull and inconspicuous except in the bordering of the inferior margins of the thoracic segments; they are mostly found in large blotches of very irregular form on the sides of the pronotum and in smaller lateral and dorsal anterior spots on the other segments, sometimes confluent and the lateral often crossing the abdominal segments; there is sometimes an interrupted mediodorsal thread; legs luteous, much infuscated especially on either side of the femoro-tibial articulation, the hind femora very broadly marked with blackish fuscous in a scalariform pattern. The antennæ are slender and about three times as long as the body, and the legs slender but not very long. Fore femora no stouter than the middle pair, much less than half as long as the hind femora and only about a sixth longer than the pronotum, the inner carina with a long preapical spine sometimes accompanied by a shorter one. Middle femora with 2–3 spines, the preapical long on the front carina, the hind carina with a very long genicular spine and sometimes an additional shorter one. Hind femora considerably more than twice as long as the fore femora, about as long as the body, the upper margin more arcuate than the lower moderately slender, about three and a quarter times longer than broad, less than the apical fourth subequal, the surface with no raised points, the outer carina with two or three very feeble distant serrulations in the apical third (♂) or unarmed (♀), the inner carina with distant raised points, the intervening sulcus narrow. Hind tibiæ straight in both sexes, very slender, slightly longer than the femora, armed beneath with 1–2 median spines besides the apical pair; spurs subopposite, the basal at the end of the proximal fourth of the tibia or a little beyond it, usually fully twice as long as the tibial depth, set at an angle of about 60° with the tibia and divaricating about 130° (rather less in the ♀), their tips incurved; inner middle calcaria considerably longer than the outer, more than twice as long as the others, about twice as long as the spurs and a little longer than the first joint of the tarsi. Hind tarsi more than two fifths as long as the tibiæ, the first joint as long as the others combined, the second more than twice as long as the third and with it as long as the fourth. Cerci tapering throughout, but especially in the basal half, nearly as long as the femoral breadth. Ovipositor fully two thirds as long as the hind femora, straight, tapering strongly in basal half, beyond equal and slender, the tip strongly upcurved and very acute, the teeth aculeate, arcuate.

Length of body, ♂ 11 mm., ♀ 14 mm.; pronotum, ♂ 3.9 mm., ♀ 4.25 mm.; fore femora, ♂ 4.5 mm., ♀ 5 mm.; hind femora, ♂ 10.5 mm., ♀ 11 mm.; hind tibiæ, ♂ 11 mm., ♀ 11.4 mm.; ovipositor, 7.5 mm.

4 ♂, 5 ♀. Lincoln, West Point, and Chadron, Dawes Co., Nebr. (L. Bruner, Corn. Univ.); Sedgwick Co., Kans., S. S. Tucker (Univ. Kans., through L. Bruner); Gulf Coast of Texas, S. F. Aaron. Osborn also reports it from Iowa.

Mr. Bruner has also sent me from Carrizo Springs, Texas, two males of a much larger size, in which the body is almost completely infuscated, so that the markings of the thorax cannot or can scarcely be seen. The following measurements are taken from one of them: length of body, 16.5 mm.; pronotum, 5.5 mm.; fore femora, 6.9 mm.; hind femora, 15.5 mm.; hind tibiæ, 16.5 mm.

39. CEUTHOPHILUS AGASSIZII.

Rhaphidophora agassizii Scudd.!, Proc. Bost. Soc. Nat. Hist., viii. 11 (1861).

Ceuthophilus agassizii Scudd.!, Bost. Journ. Nat. Hist., vii. 439 (1862); Walk., Cat. Derm. Salt. Brit. Mus., i. 202 (1869); Brunn., Monogr. Stenop., 65 (1888).

Ceuthophilus zonarius Walk., Cat. Derm. Salt. Brit. Mus., i. 203 (1869).

Body luteous, more or less infuscated in irregular patches which especially form broad bands on the posterior margins of the segments and leave the pronotum irregularly blotched, the fuscous portions occupying the anterior and posterior and usually also the lateral margins, sometimes broken along the middle line, and running backward from the anterior margins in a pair of large subdorsal stripes, the fuscous portions often dotted with distinct luteous dots. The hind femora are marked in the usual compound scalariform manner with fuscous, which unites distally in two elongate patches on the lower half of the outer surface. Antennæ more than twice as long as the body, not very slender. Legs moderately long. Fore femora distinctly broader than the middle femora, a fifth longer than the pronotum, and at least in the ♂ considerably less than half as long as the hind femora, the inner carina with a preapical spine, and at least in the ♂ with 3 or 4 other unequal spines. Middle femora with 4–5 unequal spines on the front carina besides a preapical spine, and on the hind carina numerous unequal spines, especially in the male, besides a rather long genicular spine. Hind femora as long as the body, stout, the apical fifth subequal, about three times as long as broad, with scattered raised points on the distal half, especially above, the outer carina with a tolerably uniform series of very short spines or serrations, the inner carina with similar but finer serrations. Hind tibiæ of the same length as the femora or (♂) scarcely longer, straight in both sexes or feebly sinuate in old males, moderately stout, armed beneath with 1–2 preapical spines besides the apical pair; spurs subopposite, about the length of the tibial depth, set at an angle of 35–40° with the tibia and divaricating about 80°, their tips incurved; inner middle calcaria a little longer than the outer, fully half as long again as the others or as the spurs, but much shorter than the first tarsal joint. Hind tarsi about two fifths the length of the hind tibiæ, the first joint about as long as the rest together, the second twice as long as the third and with it shorter than the fourth. Cerci tapering regularly, from a half to two thirds as long as the femoral breadth. Ovipositor fully two thirds as long as the hind femora, rather slender and equal in the distal half, the distal teeth of the inner valves long, slender, and arcuate, the proximal obsolescent.

Length of body, ♂ 17 mm., ♀ 12.5 mm.; antennæ, ♂ circ. 36 mm.; pronotum, ♂ 6.25 mm., ♀ 4.6 mm.; fore femora, ♂ 7.5 mm., ♀ 6.2 mm.; hind femora, ♂ 18 mm., ♀ 12.5 mm.; hind tibiæ, ♂ 18.5 mm., ♀ 12.5 mm.; ovipositor, 9.5 mm.

10 ♂, 1 ♀. Islands in the Gulf of Georgia, between Vancouver Isl. and the State of Washington, A. Agassiz; Vancouver Isl., H. Edwards; Oregon; British Columbia, G. W. Taylor in Bruner's coll. Through misunderstanding Brunner von Wattenwyl has credited this also to the *State* of Georgia.

40. CEUTHOPHILUS MEXICANUS, sp. nov.

Pallid, probably in life luteous, heavily overlaid with dark fuscous markings; pronotum mostly fuscous, with a mediodorsal luteous thread, expanding near anterior and posterior margins into a small rhomboid spot and with a large posterior central luteous spot in the middle of each side, the extreme inferior margin also luteous; meso- and metanotum with a large central luteous spot on either side often reaching the border posteriorly and a posterior median similar spot, the two sometimes confluent and often very irregular; abdominal segments, when darkest, with a large luteous spot on each side and a median anterior one, but the fuscous is often largely reduced; legs luteous, more or less infuscated, especially on the distal halves of the fore and middle femora, the hind femora rather heavily marked with fuscous in a scalariform pattern. Antennæ very slender, at least three times as long as the body, the legs slender and rather long. Fore femora scarcely stouter than middle femora, a fourth longer than the pronotum and half as long as the hind femora, the inner carina with two spines, both long but especially the subapical. Middle femora with 1–2 spines besides a very long subapical spine on the front carina, and the hind carina with 1–2 spines besides a long genicular spine. Hind femora as long as the body and twice as long as the fore femora, rather stout at base but slender in the distal third, nearly three times as long as broad, with a few feeble raised points on the distal half of the extreme upper surface, the outer carina with 1–4 very small distant spines on the apical half, the inner carina with 8–10 minute points, the intervening sulcus narrow. Hind tibiæ straight, slender, somewhat longer than the femora, armed beneath with a single subapical spine besides the apical pair; spurs subopposite, the basal at the end of the proximal fourth of the tibia, considerably longer than the tibial depth, set at an angle of 35–40° with the tibia and divaricating about 100°, their tips incurved: inner middle calcaria considerably longer than the outer, more than twice as long as the others or as the spurs, and nearly or quite as long as the first tarsal joint. Hind tarsi about two fifths the length of the tibiæ, the first joint as long as the rest together, the second fully twice as long as the third and with it rather longer than the fourth. Cerci rather long and tapering, fully as long as the femoral breadth.

Length of body, 10 mm.; pronotum, 4 mm.; fore femora, 5 mm.; hind femora, 9.8 mm.; hind tibiæ, 10.5 mm.

6 ♂. San Pedro, Cohahuila, Mexico, May 20; San Lorenzo, Cohahuila, Mexico, found in a cave among mummies, E. Palmer.

41. CEUTHOPHILUS PALLESCENS.

Ceuthophilus pallescens Brun.!, Can. Ent., xxiii. 37–38 (1891); Id.!, Publ. Nebr. Acad. Sc., iii. 32 (1893).

Very pallid luteous, marked with fuscous and blackish fuscous, the latter in the posterior bordering of all the segments, the former in obscure blotches on the pronotum and along its front margin, more obscure in some specimens than in others; a mediodorsal luteous thread breaks most of the fuscous markings of the body; the legs are very pallid luteous, sometimes infuscated on the distal portions of the femora and especially in scalariform markings, never deep, upon the hind femora; the spines of the legs are all dusky tipped; eyes black. The antennæ are slender and from twice to thrice the length of the body, and the legs are rather long and slender. Fore femora scarcely if any broader than the middle femora, about a fifth longer than the pronotum and half as long as the hind femora, the inner carina with a subapical spine sometimes accompanied by a shorter spine. Middle femora with 4–5 delicate spines, the subapical longer than the others on the front carina, and on the hind a similar series besides a not very long genicular spine. Hind femora much shorter than the body, twice as long as the fore femora, rather slender, being about three and a half times longer than broad, tapering pretty regularly to the tip with no genicular swelling, the surface with a few very scattered raised points especially on the inner side and above beyond the middle, both carinæ minutely and rather distantly serrulate, the intervening sulcus slender. Hind tibiæ straight in both sexes, considerably longer than the femora, rather slender, apically armed beneath with a series of three recumbent spines besides the apical pair; spurs subopposite, the basal beyond the end of the proximal third of the tibia, fully as long as the tibial depth, set at an angle of about 50° with the tibia and divaricating about 90°, feebly incurved at tip; inner middle calcaria considerably longer than the outer, twice as long as the others and nearly twice as long as the spurs, but very much shorter than the first tarsal joint. Hind tarsi fully two fifths the length of the tibia, the first joint fully equal to the rest together, the second twice as long as the third and with it as long as the fourth. Cerci slender and regularly tapering, about as long as the femoral breadth. Ovipositor of exceptional length, being nearly as long as the hind femora, very feebly arcuate, slender throughout but especially beyond the proximal third, the tip scarcely upturned more than the uniform arcuation and produced to an angle of only about 40°, the teeth of the inner valves more distant than usual, aculeate but not long, arcuate.

Length of body, ♂ 8.5 mm., ♀ 18 mm.; pronotum, ♂ 3 mm., ♀ 5 mm.; fore femora, ♂ 3.5 mm., ♀ 6.1 mm.; hind femora, ♂ 7.5 mm., ♀ 12 mm.; hind tibiæ, ♂ 8 mm., ♀ 13.5 mm.; ovipositor, 11.25 mm.

1 ♂, 2 ♀. Hat Creek, Nebr., in wells; Pine Ridge, Nebr., Aug. 4, under timber; Hecla, Wyo.; all from L. Bruner. The ♂ from Pine Ridge is rather immature.

42. CEUTHOPHILUS SYLVESTRIS.

Ceuthophilus sylvestris Brun.!, Bull. Washb. Coll., i. 126–127 (1885).

Nearly uniform mahogany brown, glabrous, very faintly and broadly infuscated at the hinder margins of all the segments and on the front margin of the pronotum, the lateral margins of the thoracic segments very faintly bordered with obscure luteous; legs uniformly of a lighter tint than the body, the hind femora without scalariform markings. Antennæ slender, more than twice as long as the body, the legs moderately short. Fore femora no stouter than the middle femora, scarcely longer than the pronotum, half as long as the hind femora, the inner carina with a short subapical spine. Middle femora with only a single small spine or occasionally a second on either carina besides the posterior genicular spine. Hind femora moderately stout, tapering regularly to the tip with no pregenicular constriction or genicular enlargement, fully three times as long as broad, twice as long as the fore femora, with no raised points upon the surface, both carinæ (♀) with the most delicate possible uniform and not crowded serrulation, the intervening sulcus narrow. Hind tibiæ considerably longer than the femora, slender; if armed beneath, so slightly as not to be seen with an ordinary hand-glass; spurs subopposite, the basal at about the end of the proximal third of the tibia, rather longer than the tibial depth, set at an angle of about 35° with the tibia and divaricating about 70°, their tips scarcely incurved; inner middle calcaria considerably longer than the outer, twice as long as the others or as the spurs, but shorter than the first tarsal joint. Hind tarsi almost half as long as the tibiæ, the first joint not so long as the others combined, the second about twice as long as the third and with it shorter than the fourth. Cerci slender, tapering, finely pointed, slightly longer than the femoral breadth. Ovipositor straight, considerably more than two thirds as long as the hind femora, gently tapering in proximal, slender in distal half, the tip upturned to an excessively fine point, the teeth produced, triangular, subaculeate.

Length of body, ♀ 7 mm.; pronotum, 3 mm.; fore femora, 3.1 mm.; hind femora, 6.1 mm.; hind tibiæ, 7 mm.; ovipositor, 4.4 mm.

2 ♀. Topeka, Kans., F. W. Cragin, through L. Bruner.

43. CEUTHOPHILUS CRASSUS, sp. nov.

Specimens preserved after immersion in alcohol are dark fuscous and very dull castaneous, the former prevailing, the latter seen on the anterior borders of the abdominal segments in a median thoracic line, irregular transverse bands on the middle of the meso- and metanotum, and irregular blotches on the pronotum, mostly sublinear and very angular; the legs are prevailingly dusky except at base. Antennæ imperfect in all specimens but probably twice as long as the body. Legs rather short. Fore femora distinctly broader than the middle femora, but little longer than the pronotum and much less than twice as long as the hind femora, the inner carina with two small semi-recumbent spines, one of them subapical. Middle femora with 3–4 small spines on the inner carina, one subapical, and on the hind carina 3–4 similar spines besides a small genicular spine. Hind femora considerably more than twice as long as the fore femora, much shorter than the body, stout, tapering to the tip with no pregenicular constriction, scarcely more than two and a half times longer than broad, with a very few scattered raised points on the upper surface apically, the outer carina finely and sparsely serrulate throughout, more densely in the ♂ than in the ♀, the inner carina similar, the intervening sulcus narrow. Hind tibiæ straight in both sexes, scarcely or no longer than the femora, moderately stout, armed beneath with a single subapical spine besides the apical pair; spurs subopposite, the basal pair at the end of the proximal fourth of the tibia, not much longer than the tibial depth, set at an angle of 30–40° with the tibia and divaricating about 60°, faintly incurved; inner middle calcaria somewhat longer than the outer, nearly twice as long as the others, twice as long as the spurs, and as long as the first tarsal joint. Hind tarsi much less than half as long as the tibiæ the first joint hardly equalling the rest taken together. the second twice as long as the third and with it a little shorter than the fourth. Cerci rather short and slender. Ovipositor two thirds the length of the hind femora, rapidly tapering at base, the distal half slender, the armature of the inner valves acicular, arcuate.

Length of body, ♂ 13 mm., ♀ 17.5 mm.; pronotum, ♂ 4.5 mm., ♀ 5.6 mm.; fore femora, ♂ 5 mm., ♀ 6 mm.; hind femora, ♂ 11.25 mm., ♀ 13.5 mm.; hind tibiæ, ♂ 11.5 mm., ♀ 13.5 mm.; ovipositor, 9 mm.

1 ♂, 3 ♀. Locality unknown; probably from one of the Southwestern States. It is a very robust species.

44. CEUTHOPHILUS PINGUIS, sp. nov.

Of mingled fuscous and luteo-castaneous, sometimes one, sometimes the other prevailing: when it is the latter, the fuscous shows itself on either side of the mediodorsal line in a series of subtriangular subdorsal patches seated upon the posterior margin of the segments, much larger on the thoracic than on the abdominal and partially or wholly absent from some of the latter; besides there is a series of lateral blotches, just failing to reach the lower margins of the nota and more extended on each segment anteriorly than posteriorly; on the pronotum these two sets blend irregularly, so that here the darker colors prevail; the hind femora are more or less infuscated with the markings common to the genus, more or less distinct, the geniculations laterally blackish. Antennæ moderately stout. Legs not very elongate. Fore femora basally somewhat stouter than the middle femora, considerably less than half as long as the hind femora, about a fourth longer than the pronotum, the inner carina with 2–3 spines, the subapical and sometimes one or both the others pretty large. Middle femora with the front carina as in the fore femora, the hind carina with 1–2 spines near the middle besides a very long genicular spine. Hind femora a little shorter than the body, considerably more than twice as long as the fore femora, very stout and broad, being considerably less than three times as long as broad, with a preapical broad constriction, so that the distal fourth is subequal, the apical half covered very sparsely except beneath with raised spinous points of a reddish color, the outer carina armed with 3–4 very small subequal irregularly distant spines, the inner with a dozen spinules irregularly placed, the intervening sulcus not very broad. Hind tibiæ straight, about a tenth longer than the femora, armed beneath with a single preapical spine besides the apical pair; spurs subopposite, the basal at end of basal fourth of the tibia, fully twice as long as the tibial depth, set at an angle of about 30° with the tibia and divaricating scarcely more than 90°, their tips incurved distinctly; inner middle calcaria twice or more than twice as long as the others or as the spurs and as long as or longer than the first tarsal joint. Hind tarsi fully two fifths the length of the tibiæ, the first joint almost or quite as long as the rest together, the second more than twice as long as the third and with it as long as the fourth. Cerci pretty stout at base, tapering delicately, probably as long as the femoral breadth (broken in all specimens seen).

Length of body, 16 mm.; antennæ, 28+ mm.; pronotum, 5.1 mm.; fore femora, 6.5 mm.; hind femora, 14.6 mm.; hind tibiæ, 16 mm. One imperfect specimen is nearly half as large again.

4 ♂. Eagle Pass, Texas, C. O. Schott.

45. CEUTHOPHILUS INQUINATUS, sp. nov.

Ceuthophilus divergens Brun.! (pars), Publ. Nebr. Acad. Sc., iii. 32 (1893).

Deep blackish fuscous, almost black, marked slenderly with luteous which dorsally is tinged with reddish; there is a mediodorsal line, expanding near the posterior margin of the pronotum, on the middle of the meso- and metanotum, and on the anterior margin of the abdominal segments into small subtriangular or sublozenge-shaped patches, and crossed near the anterior margin of the pronotum by a short transverse bar sometimes forming a rhomb; the sides of the segments and particularly of the pronotum are marked in the middle by irregular luteous blotches and the lateral margins of the thoracic segments are bordered with the same more or less conspicuously; the hind femora are dark luteous with heavy scalariform markings of black and with longitudinal streaks of blackish fuscous on either side of the submedian clear stripe apically; other femora luteous like the rest of the legs, but more or less infuscated, especially apically. Antennæ moderately slender and probably long; legs moderately long. Fore femora not stouter than middle femora, less than a fourth longer than the pronotum and distinctly less than half as long as the hind femora, the inner carina with a very long subapical spine, sometimes accompanied by one or two others. Middle femora with the front carina armed as in the fore femora, the hind carina the same but the apical spine genicular and very long. Hind femora broad but not heavy, scarcely more than three times as long as broad, tapering rather rapidly so that the distal fourth is subequal, considerably more than twice as long as the fore femora, with half a dozen raised points on the upper surface beyond the middle, the outer carina with four or five serrations next the narrowest portion of the femora and before it half a dozen widely separated inequidistant spines, of which two or three just beyond the middle of the femora are larger than the others and rather coarse, the longest no longer than the tibial spurs (♂) or wholly unarmed except for two or three inconspicuous pregenicular spinules (♀), the inner carina with a series of rather distant slight spinules, slighter and less frequent in the ♀ than in the ♂, the intervening sulcus moderate. Hind tibiæ straight in both sexes or with the faintest possible arcuation in the ♂, distinctly though not greatly longer than the femora, armed beneath with a single preapical spine, besides the apical pair; spurs subalternate, the basal placed before the end of the proximal fourth of the tibia, nearly or quite twice as long as the tibial depth, set at an angle of about 50° with the tibia and divaricating about 110°, their tips feebly incurved; inner middle calcaria but little longer than the outer, considerably more than twice as long as the others, nearly twice as long as the spurs, and slightly longer than the first tarsal joint. Hind tarsi two fifths the length of the tibiæ, the first joint about as long as the rest together, the second twice as long as the third and with it about the length of the fourth. Cerci rather stout at base, tapering beyond, not so long as the femoral breadth. Ovipositor more than three fifths the length of the hind femora, straight, tapering on proximal half or less, beyond moderately slender, the tip upturned and produced to an extremely acute point, the teeth of the inner valves aculeate and more or less arcuate.

Length of body, ♂ 13.5 mm., ♀ 13 mm.; pronotum, ♂ 4.3 mm., ♀ 5 mm.; fore femora, ♂ ♀ 5.5 mm.; hind femora, ♂ 12.25 mm., ♀ 12.5 mm.; hind tibiæ, ♂ 14 mm., ♀ 13 mm.; ovipositor, 8 mm.

2 ♂, 1 ♀. Fairbury, Nebr., Dr. Eaton; Lincoln, Nebr.; both through Mr. L. Bruner.

46. Ceuthophilus discolor, sp. nov.

Body blackish fuscous, almost black with luteous markings, as follows: a mediodorsal series of moderately large roundish spots, two on the pronotum and one on each of the succeeding segments more or less distinctly connected by a luteous thread; on the middle of each side of each segment a transverse dash, on the abdominal segments more elongated than on the thoracic, and generally partly merged in the mediodorsal spot, on the pronotum larger than elsewhere and accompanied by some outlying dots; also as an inferior margining of the thoracic segments; but all these markings may become so enlarged as to make the surface prevailingly luteous; the femora are fuscous, becoming lutescent toward the base, on the hind pair as heavy scalariform markings, on the anterior pairs as slender stripes. The antennæ are brownish luteous, rather slender and apparently about three times the length of the body, the legs rather short and slender. Fore femora no stouter than the middle femora, less than a fourth longer than the pronotum, much less than half as long as the hind femora, the inner carina with a long subapical spine, sometimes accompanied by another minute spine. Middle femora with a very long subapical spine accompanied by a smaller one on the front carina, and the hind carina with a long genicular spine only. Hind femora much shorter than the body, but about two and a quarter times longer than the fore femora, rather slender, being nearly three and a quarter times longer than broad, the apical fourth subequal, the surface with a few raised points scattered here and there beyond the middle of the upper half of the femora both inside and outside, the outer carina with seven or eight small unequal and inequidistant recumbent denticulations on the apical half (♂) or apparently unarmed (♀), the inner carina with some very distant and very slight serrulations, the intervening sulcus slender. Hind tibiæ straight in both sexes, distinctly longer than the femora, slender, armed beneath with a single preapical spine besides the apical pair; spurs subopposite, fully twice as long as the tibial depth, set at an angle of about 35–45° with the tibia, and divaricating about 90–100°, their tips considerably incurved; inner middle calcaria scarcely longer than the outer, more than twice as long as the others, nearly twice as long as the spurs and about as long as the first tarsal joint. Hind tarsi two fifths the length of the tibiæ, the first joint fully as long as the rest together, the second more than twice as long as the third and with it nearly or quite as long as the fourth. Cerci rather slender, tapering regularly, about as long as the femoral breadth. Ovipositor more than two thirds as long as the hind femora, straight, beyond the proximal third very slender, the tip upturned abruptly and produced to an aculeate point, the teeth of the inner valves aculeate, pretty long and arcuate.

Length of body, ♂ 10.5 mm., ♀ 12.5 mm.; pronotum, ♂ 3.5 mm.,

♀ 3.75 mm.; fore femora, ♂ 4.25 mm., ♀ 4.1 mm.; hind femora, ♂ ♀ 9.5 mm.; hind tibiæ, ♂ ♀ 10.5 mm.; ovipositor, 6.75 mm.

1 ♂, 1 ♀. West Point, Nebr., L. Bruner; Ellis, Kansas, Watson (Mus. Comp. Zoöl.).

47. CEUTHOPHILUS PALLIDUS.

Ceuthophilus pallidus Thom.!, Ann. Rep. U. S. Geol. Geogr. Surv. Terr., v. 434 (1872); Id., Proc. Dav. Acad. Nat. Sc., i. 264 (1876); Glov., Ill. N. A. Ent., Orth., pl. 18, fig. 18 (1874); Towns., Can. Ent., xxiv. 197–198 (1892); [Ril.], Ins. Life, i. 282–283 (1893); Towns., Ins. Life, vi. 58 (1893).

Body bright luteous, heavily marked with blackish fuscous; on the pronotum the markings are very irregular, but consist in the main of the following: on either side of the front margin a large transverse fuscous spot, which reaches neither the mediodorsal line nor the lateral margin and is interrupted below by a roundish spot and above by the incursion from the anterior margin of a short narrowing dash; in the middle of the dorsum a quadrate spot divided by a mediodorsal luteous line into a pair of longitudinal bars, each connected anteriorly with the before mentioned anterior spot, and leaving a luteous submarginal anterior mediodorsal spot; an infero-posterior black spot not touching the margin; and a laterodorsal subtriangular spot on the posterior margin; on the succeeding thoracic segments, and on the abdominal there is a series of large irregularly triangular laterodorsal spots on the posterior margins, and another lateral series of roundish or transverse spots generally not reaching any margin; the legs are luteous, the fore and middle femora more or less infuscated in longitudinal streaks, the hind femora dull luteous with scalariform fuscous markings. Antennæ moderately slender, about twice the length of the body, the legs moderately long. Fore femora scarcely stouter than the middle femora, less than a fifth longer than the pronotum, much less than half as long as the hind femora, the inner carina with a tolerably long subapical spine sometimes accompanied by another minute one. Middle femora with a long subapical spine on the front carina, accompanied at least in the male by a couple of others smaller, and on the hind carina one or two short spines at least in the male, accompanied by a long genicular spine. Hind femora moderately slender, fully three times as long as broad, two and a third times longer than the fore femora, the surface with a few scattered raised points on the distal half and especially along the upper edge of the inner surface, the outer carina with 6–8 very unequal and inequidistant spines, the longest about as long as the tibial spurs (♂) or wholly unarmed or with a few raised points apically (♀), the inner carina very distantly and subequidistantly serrulate, finer in the ♀ than in the ♂, the intervening sulcus moderate. Hind tibiæ straight in both sexes, slightly longer than the femora, armed beneath with a single subapical spine, besides the apical pair; spurs subalternate, the basal near the end of the proximal fourth of the tibia, about half as long again as the tibial depth, set at a varying angle with the tibia, the outer series at least in the ♂ being directed outward, the inner series both inward and posteriorly, divaricating about 120°, the tips incurved; inner middle calcaria considerably longer than the outer, more than twice as long as the others or as the spurs, and nearly as long as the first joint of the tarsi. Hind tarsi fully two fifths as long as the tibiæ, the first joint fully as long as the remaining joints together, the second three times as long as the third and with it as long as the fourth. Cerci very slender and tapering in their distal half, stouter and subequal in their proximal half, scarcely so long as the femoral breadth. Ovipositor about half as long as the hind femora, straight, slender and equal beyond the basal third, the tip produced, acuminate and upturned, the teeth long, aculeate, arcuate.

Length of body, ♂ 15 mm., ♀ 12 mm.; pronotum, ♂ ♀ 4.5 mm.; fore femora, ♂ 5.25 mm., ♀ 5.1 mm.; hind femora, ♂ 12.2 mm., ♀ 11.5 mm.; hind tibiæ, ♂ 13.1 mm., ♀ 12 mm.; ovipositor, 5.5 mm.

1 ♂, 3 ♀. Hot Springs, Dak.; Denver, Col., Beales; Las Cruces, N. Mex., C. H. T. Townsend; Silver City, N. Mex., C. H. Marsh; — all through L. Bruner. In the U. S. National Museum, mostly from the Riley collection, are 2 ♂, 5 ♀, from Laramie and Red Buttes, Wyo., Custer, Colorado (Cockerell), Colorado, and New Mexico. Thomas reported it from S. E. Colorado, Empire, Col., and Red Buttes, Wyo.; Townsend from Colorado and New Mexico.

48. CEUTHOPHILUS VINCULATUS, sp. nov.

Pale testaceous, nearly uniform, the posterior margins of all the segments infuscated, the apices of the hind femoral geniculations touched with fuscous, and the pronotum more or less blotched with pale fuscous, particularly with a pair of short submedian stripes on the anterior half. Antennæ slender and nearly three times as long as the body, the legs short but not stout. Fore femora distinctly stouter than the middle femora, but very little longer than the pronotum, less than half as long as the hind femora, the inner carina with a preapical spine. Middle femora with 1–4 spines on the inner carina, and on the hind carina 1–2 spines besides the genicular spine. Hind femora moderately stout, tapering regularly to the very tip with no pregenicular contraction, considerably more than twice as long as the fore femora, less than three times as long as broad, glabrous, with no raised points on any part, the outer carina pretty uniformly and finely serrate, especially in apical half, the inner carina similarly but more sparsely serrate, the intervening sulcus narrow except distally. Hind tibiæ straight in both sexes, slender, no wider in the middle than at base, equal to or scarcely so long as the hind femora, armed beneath with one or two preapical spines besides the apical pair; spurs subopposite, not so long as the tibial depth, set at an angle of about 45° with the tibia and divaricating at even a less angle the extreme tips incurved; inner middle calcaria scarcely longer than the outer, nearly twice as long as the others or as the spurs, and much shorter than the first joint of the tarsi. Cerci rather stout, tapering, about two thirds as long as the femoral breadth. Ovipositor rather stout and uniformly tapering on the basal half, uniform and slender on the distal half, somewhat longer than the fore femora, the extreme tip prolonged to a spine, the teeth of the inner valves aciculate, arcuate.

Length of body, ♂ 12 mm., ♀ 13 mm.; antennæ, ♂ (est.) 30 mm.; pronotum, ♂ 3.75 mm., ♀ 3.6 mm.; fore femora, ♂ 4.2 mm., ♀ 4 mm.; hind femora, ♂ 9 mm., ♀ 7.65 mm.; hind tibiæ, ♂ 8.5 mm., ♀ 7.65 mm.; ovipositor, 5 mm.

4 ♂, 1 ♀. Nevada, H. Edwards; North Pacific R. R. Survey below Lake Jessie at Fort Benton, Dr. Suckley. Since description I have received 2 ♂, 5 ♀. from West Point, Lincoln, and Holt Co., Nebraska, from L. Bruner; and have seen in the Museum of Comparative Zoölogy at Cambridge a ♂ and ♀ from Santa Barbara, Cal. (Osten Sacken), which apparently belong here, although there are no indications of any transverse banding. There are also 2 ♂ in the U. S. National Museum from California and Washington, both from the Riley collection.

This species is closely allied to *C. californianus*, but has slenderer hind tibiæ and a longer ovipositor; its general appearance is very similar.

49. CEUTHOPHILUS TESTACEUS, sp. nov.

Light fusco-testaceous, with a faint mediodorsal luteous stripe and obscurely dotted with luteous (sometimes obsolete), the lower sides of the body growing gradually pallid luteous, and the pronotum more or less mottled or clouded with fuscous; legs testaceous, sometimes slightly infuscated, the hind femora with feeblest possible fuscous scalariform markings. Antennæ very slender, two or three times as long as the body, the legs short. Fore femora slightly broader than the middle femora, a very little longer than the pronotum (relatively longer in the ♀ than in the ♂), a little more than half as long as the hind femora, the inner carina with a rather long subapical spine and sometimes an additional one. Middle femora with 2–4, usually three, subequal spines on the front carina, and on the hind carina generally four spines besides a moderately long genicular spine. Hind femora moderately slender, tapering with almost exact regularity to the tip, somewhat more than three times as long as broad, rather less than twice as long as the fore femora, the surface just beyond the middle with very scattered raised points on the whole upper half of the femora outside and inside, both carinæ distantly and delicately serrulate in both sexes, the intervening sulcus narrow. Hind tibiæ straight in both sexes, a very little longer than the femora, at least in the male, slightly enlarged apically as viewed from the side, armed beneath with a single subapical spine besides the apical pair; spurs subalternate, the basal set far before the end of the proximal fourth of the tibia, fully twice as long as the tibial depth, set at an angle of 30–40° with the tibia and divaricating at not above 90°, their extreme tips scarcely incurved; inner middle calcaria of about the same length as the outer, nearly twice as long as the others and half as long again as the spurs, but shorter than the first joint of the tarsi. Hind tarsi almost half as long as the tibiæ, the first joint as long as the rest together, the second more than twice as long as the third and with it equal to the fourth. Cerci moderately slender, at least as long as the pronotum. Ovipositor slender, straight, tapering at the base, equal from before the middle, longer than the fore femora, the tip produced to an aculeate spine projecting a little upward, the teeth of the inner valves pretty long, aculeate, arcuate.

Length of body, ♂ 10 mm., ♀ 9 mm.; pronotum, ♂ 4 mm., ♀ 3.6 mm.; fore femora, ♂ 4.25 mm., ♀ 4.2 mm.; hind femora, ♂ 8 mm., ♀ 7.7 mm.; hind tibiæ, ♂ 8.5 mm., ♀ 7.8 mm.; ovipositor, 4.5 mm.

2 ♂, 2 ♀. West Point, Nebr.; Sheridan, Wyo., C. Y. Smith, all from L. Bruner; St. Louis, Engelmann.

50. CEUTHOPHILUS CALIFORNIANUS.

Ceuthophilus californianus Scudd.!, Bost. Journ. Nat. Hist., vii. 438 (1862); Walk., Cat. Derm. Salt. Brit. Mus., i. 202 (1869).

Ceuthophilus castaneus Thom.!, Rep. U. S. Geol. Geogr. Surv. Terr.,

v. 435 (1872); Glov., Ill. N. A. Ent., Orth., pl. 18, fig. 17 (1874); Fletch., Rep. Exp. Farms Can., 1888, 63 (1889).

Ceuthophilus denticulatus Scudd.!, Ann. Rep. Geogr. Surv. West 100th Mer., 1876, 279 (1877).

Varying from light to dark castaneous with very feeble markings, excepting usually a greater or less degree of infuscation along the posterior margins of all the segments and the anterior margin of the pronotum; the pronotum is also sometimes feebly enlivened with vermiculate fuliginous markings and not infrequently a faint luteous line may be traced along the middle of the dorsum, often conspicuous on the pronotum and always slender; the legs are concolorous with the body. The antennæ are rather coarse, tapering throughout uniformly, the eyes small, distinctly smaller than the antennal scrobes, the legs short and stouter than usual. Fore femora distinctly stouter than the middle femora, arched superiorly, about a fifth longer than the pronotum and slightly more than half as long as the hind femora, the inner carina with a single subapical spine besides being minutely serrulate throughout. Middle femora having a variable number of spines but usually 3–4 on the front carina, and on the hind carina a variable but generally considerable number of minute spines or serrations besides a short genicular spine. Hind femora about two thirds as long as the body (♂) or a little less than that (♀), almost twice as long as the fore femora, moderately stout, regularly tapering to the very apex with no pregenicular constriction, about three times as long as broad, glabrous, with a few feeble distant raised points above just before the geniculation, the outer carina uniformly and rather delicately serrulate except at base, more feebly in the female than in the male, the inner carina similarly but more delicately serrulate, the intervening sulcus tolerably broad apically but not at base. Hind tibiæ of male straight, unusually stout, on the upper surface twice as broad in the middle as at base, of the same length as the femora, armed beneath with a single preapical spine besides the apical pair; spurs subopposite, about equal to or a little longer than the tibial depth, set at an angle of about 45° to the tibia and diverging at an angle of 60° or less with each other, their tips incurved; inner middle calcaria slightly longer than the outer, half as long again as the other calcaria, twice as long as the spurs and nearly as long as the first joint of the tarsus. Hind tarsi nearly half as long as the tibiæ, the first joint nearly as long as the others combined, the second twice as long as the third and with it not so long as the fourth. Cerci rather stout, tapering throughout, not much longer than half the femoral breadth. Ovipositor as long as the pronotum, tapering in the basal half, beyond equal, not very slender and straight, the tip strongly upcurved, the armature of the inner valves formed of long, bluntly pointed, arcuate teeth.

Length of body, ♂ 19 mm., ♀ 16.25 mm.; antennæ, ♂ (est.) 40 mm.; pronotum, ♂ 5.25 mm., ♀ 4.75 mm.; fore femora, ♂ 6.75 mm., ♀ 5.3 mm.; hind femora and tibiæ, each, ♂ 13 mm., ♀ 10.25 mm.; ovipositor 4.75 mm.

19 ♂, 4 ♀. California (Edwards, Behrens, Crotch, Osten Sacken, Palmer, Bruner), and in particular San Francisco, Pescadero, Gilroy, Sonoma and Marin Counties, Santa Barbara, June, and San Bernardino, Feb.; Beaver Dam, south of St. George, Utah, in the most desert region, April 20–28, E. Palmer; Ehrenberg, Colorado River, Arizona, E. Palmer. It has also been reported from Vancouver Isl. by Walker and Fletcher. In the U. S. National Museum, from the Riley Collection, are 4 ♂ from California, Martinez, Cal. (Turner), Los Angeles Co., Cal., and no locality (A. E. Brush); also a single ♂ with extraordinarily broad hind tibiæ from Alameda Co., Cal.

51. CEUTHOPHILUS LATIPES, sp. nov.

Nearly uniform dull luteo-testaceous, with the usual fuscous slender scalariform markings on the hind femora and short longitudinal fuscous dashes on the posterior portions of the abdominal segments, repeated vaguely as cloudy markings on the meso- and metanotum; pronotum slightly infuscated anteriorly and posteriorly. Antennæ moderately slender, the legs exceptionally short. Fore femora distinctly though only slightly stouter than the middle femora, scarcely longer than the pronotum and much less than half as long as the hind femora, the inner carina unarmed. Middle femora with a single preapical spine on the front carina, and on the hind carina a single small spine or none besides a tolerably long genicular spine. Hind femora somewhat shorter than the body, exceptionally broad, about two and a half times longer than broad, almost two and a half times longer than the fore femora, strongly arcuate beneath, strongly and sharply constricted before the geniculation, with a very few raised points on the middle of the inner side above, the outer carina closely serrulate, the inner carina distantly and finely denticulate, the intervening sulcus moderately broad and uniform. Hind tibiæ with the extreme base briefly arcuate, beyond straight, of the same length as the femora, slender, armed beneath with a single delicate subapical spine (sometimes two) besides the apical pair; spurs opposite, the basal at the end of the proximal third of the tibia, scarcely longer than the tibial breadth, set at an angle of about 60° with the tibia and divaricating about 80°, their tips incurved; inner middle calcaria considerably longer than the outer, fully half as long again as the others or as the spurs, but much shorter than the first joint of the tarsi. Hind tarsi considerably less than half as long as the tibiæ, the first joint hardly so long as the rest together, the second fully twice as long as the third and with it as long as the fourth. Cerci rather stout, tapering rapidly, somewhat shorter than the breadth of the femora.

Length of body, 11 mm.; antennæ, 13+ mm.; pronotum, 3.25 mm.; fore femora, 3.65 mm.; hind femora, 9 mm.; hind tibiæ, 9 mm.

1 ♂, Sierra de la Miguelito Mexico, E. Palmer.

52. CEUTHOPHILUS PACIFICUS.

Ceuthophilus pacificus Thom.. Ann. Rep. U. S. Geol. Surv. Terr., v. 436 (1872); Glov., Ill. N. A. Ent., Orth., pl. 14, fig. 8 (1872).

Ceuthophilus unispinosus Brunn., Monogr. Stenop., 64 (1888).

Luteous, heavily irrorate with more or less confluent fuscous dots, giving it, as Thomas well expresses it, a mossy appearance; the amount of confluence and accordingly of infuscation varies somewhat in different individuals, and is usually deepest on the pronotum, which also often shows on either side a larger or smaller rufo-luteous patch free from dots; the hind femora retain the usual scalariform markings, which are narrower than common. Antennæ moderately stout at base, very slender beyond, three or four times as long as the body. Legs rather short. Fore femora scarcely stouter than the middle femora, about a fourth longer than the pronotum and much less than half as long as the hind femora, the inner carina with a long subapical spine. Middle femora with a long subapical spine on the front carina sometimes accompanied by 1–2 shorter ones, the hind carina with a single subapical spine besides the genicular spine. Hind femora almost as long as the body, considerably more than twice as long as the fore femora, very stout, apically tapering rapidly especially in the ♂, the distal fifth subequal, about two and a half times longer than broad (♂), the darker portions heavily scabrous with raised points, besides a sparse sprinkling of the same on the apical half of the inner surface, the outer carina minutely and bluntly bi- or tri-serrulate, sometimes with a large preapical triangular dentiform spine serrulate on its proximal edge (♂) or unarmed (♀), the inner carina similar but in the distal half more coarsely uniserrulate, the serration stopping abruptly before the apex with a distinct denticle, sometimes produced to a stout triangular spine, serrulate on the proximal edge (♂) or with a few feeble raised points or spinules on the apical half (♀), the intervening sulcus broad and V-shaped. Hind tibiæ strongly and sharply bowed just before the middle, and on the proximal portion prominently and roundly laminate beneath, by reason of the bow no longer than the femora (♂) or straight and simple, slightly longer than the femora (♀), armed beneath with a single preapical spine and an apical pair; spurs subopposite, the basal pair but little before the middle of the tibia, about as long as the tibial depth, set at an angle of about 45° with the tibia and divaricating but little more than that, the tips feebly incurved; inner middle calcaria slightly longer than the outer, more than twice as long as the others or as the spurs, and as long as the first tarsal joint. Hind tarsi about two fifths the length of the tibiæ, the first joint fully as long as the rest together, the second nearly three times as long as the third and almost equal to the fourth. Cerci stout in the basal half, beyond tapering, not more than half as long as the femoral breadth, except in the female. Ovipositor gently tapering in the basal half, slender beyond and finely pointed, scarcely upturned at tip, about two thirds as long as the hind femora, the inner valves feebly and bluntly serrulate apically with no apical hook.

Length of body, ♂ 11.5 mm., ♀ 12.5 mm.; pronotum, ♂ 3.75 mm., ♀ 4.1 mm.; fore femora, ♂ 4.4 mm., ♀ 5 mm.; hind femora, ♂ 10 mm., ♀ 11.7 mm.; hind tibiæ, ♂ 10 mm., ♀ 12.25 mm.; ovipositor, 7.5 mm.

9 ♂, 13 ♀. California, P. R. Uhler, J. Akhurst, H. Edwards, Behrens; Nevada, H. Edwards; Mountains about Lake Tahoe, Cal., Oct., H. W. Henshaw in Capt. Wheeler's Expl., 1876. The U. S. National Museum also contains 5 ♂, 3 ♀, from Martinez, Cal., H. W. Turner, and Los Angeles Co., Coquillet and others, mostly through the collection of C. V. Riley.

The dorsal surface of the abdomen of the male of this species somewhat resembles its next neighbor, *C. henshawi*, in its sculpture, the several segments being somewhat uniformly and rather closely covered with blister-like elevations, largest and closest next the dorsal line. Neither Thomas nor Brunner has noticed this peculiarity.

53. CEUTHOPHILUS HENSHAWI, sp. nov.

Mostly brownish fuscous above, but very minutely and abundantly irrorate with luteous, increasingly so in passing down the sides, so that the luteous prevails on the flanks; the pronotum is also usually marked with a broad prevailingly luteous mesial band, and the mesonotum and metanotum often but not always with a similar broad transverse patch above; occasionally in young individuals these thoracic markings are reduced to a narrow mesial luteous stripe; the hind femora are similarly speckled in place of the usual markings, though these sometimes prevail. Antennæ very slender, probably about twice the length of the body. Legs rather short and not stout. Fore femora no stouter than the middle femora, about a fourth longer than the pronotum in the ♂, less than that in the ♀, and in both considerably less than half the length of the hind femora, the inner carina with an exceedingly minute preapical spine. Middle femora with 2–3 minute spines (sometimes obsolete in the ♀) on the front carina, and the hind carina similarly armed besides a small genicular spine. Hind femora stout and broad, the lower margin straight by the posterior elevation of the outer carina almost to the geniculation, when it terminates abruptly and subacutely, as long as the body and about three times as long as broad (♂) or stout and broad, normal, about three fourths as long as the body, with a few raised points clustered above the depressed middle line of the femora (♀), the outer carina closely serrulate throughout (♂) or simple and unarmed (♀). Hind tibiæ abruptly and considerably bent just beyond the base, but still nearly a tenth longer than the femora, beyond the bend nearly straight (♂), or straight throughout and similarly longer than the femora (♀), beneath with a series of raised points and 1–2 recumbent subapical spines besides a preapical and apical pair (♂) or with a single subapical spine and an apical pair (♀); spurs subopposite, the basal pair situated not far before the middle of the tibia, no longer than the tibial depth, set at an angle of 45° with the tibia and divaricating about 90°, their tips incurved; inner middle calcaria considerably longer than the outer, more than twice as long as the others or as the spurs, but shorter than the first tarsal joint. Hind tarsi about one half the length of the hind tibiæ, very slender, the first joint not so long as the rest together, the second fully twice as long as the third, and with it longer than the fourth. Cerci greatly swollen in the basal half. beyond slight, the whole about half as long as the femoral breadth. Ovipositor considerably less than two thirds as long as the hind femora, tapering throughout, the tip pointed but hardly upturned, the inner blades obsoletely serrulate with 7–8 elevations.

Length of body, ♂ ♀ 12 mm.; antennæ, ♂ ♀ 15+ mm.; pronotum, ♂ 4 mm., ♀ 3.5 mm.; fore femora, ♂ 5.2 mm., ♀ 4 mm.; hind femora, ♂ 11.5 mm., ♀ 8.9 mm.; hind tibiæ, ♂ 12.25 mm., ♀ 9.4 mm.; ovipositor, 5.25 mm.

6 ♂, 2 ♀. Sanzalito, Cal., California, Vancouver Isl., Washington,

H. K. Morrison, coll. S. Henshaw; 1 ♂, 4 ♀, Oregon, and Placer, Kern, and Los Angeles Counties, Cal., mostly from the Riley collection (U. S. Nat. Mus.).

The male of this species is remarkable for the surface sculpture of the dorsum of the abdomen, the first seven segments of which, but particularly the second to the sixth inclusive, are densely covered with minute strongly elevated tubercles, besides which on the anterior portion of the first to the fifth segments and almost crossing the segment is a mesial series of large slightly transverse tumid elevations, rounded anteriorly, truncate posteriorly. I have seen nothing resembling it in any other species, excepting to a less degree in its next neighbor, *C. pacificus;* this and the peculiar characteristics of the outer hind femoral carina make this a very striking species, which I take pleasure in dedicating to my colleague, Mr. Samuel Henshaw.

54. CEUTHOPHILUS DEVIUS, sp. nov.

Nearly uniform brownish testaceous, subglabrous, with very feeble infuscated obscure blotches especially upon the pronotum, and a fine mediodorsal luteous thread running the length of the body; surface, especially in ♂ and particularly on the thorax, very finely subcorrugate. The antennæ are coarse at base (beyond broken), the joints more or less thickened apically. The legs are rather short. Fore femora much less than half the length of the body, hardly a fifth longer than the pronotum, a little stouter than the middle femora and a little less than half as long as the hind femora, the inner carina with a preapical spine and a few (♀) or many (♂) spinous points; the fore tibiæ with a single median spine on the inner side above, and beneath with 3 (♀) or 4 (♂) pairs of stout spines. Middle femora with 5–6 (♀) or 8–9 (♂) spines on the front carina, the preapical small, at least in the ♂, the hind carina similarly armed and with a small genicular spine. Hind femora considerably shorter than the body, distinctly more than twice the length of the fore femora, nearly straight above in the ♂ where they are of nearly equal breadth on the proximal two thirds and are then somewhat abruptly emarginate beneath, less than three and a half times as long as broad in both sexes, the surface glabrous with no raised points excepting sparsely scattered ones on the upper surface in the middle half, the outer carina of both sexes with equal slight denticulations on the constricted portion of the femora, the inner carina with larger denticulations throughout (except at base) much larger and more unequal in the ♂, where the largest are as long as the tibial spurs, the inferior sulcus narrow. Hind tibiæ straight, of the same length as the femora, stout, basally constricted, beneath with a row of distant spines besides the apical pair; spurs subopposite, the basal pair at the end of the proximal third of the tibia, *scarcely longer than the tibial* depth, set at an angle of 45° with the tibia and divaricating 70–80°; inner middle calcaria but little longer than the outer, about half as long again as the others or as the spurs, shorter than the first joint of the tarsus. Hind tarsi about one third as long as the tibiæ, the first joint scarcely longer than the fourth and less than twice as long as the second and third together, the second but little longer than the third. Cerci rather slender, tapering throughout, pointed, much shorter than the femoral breadth. Ovipositor nearly straight, scarcely longer than the fore femora, the basal *half tapering, the apical slender and equal, the tip pretty strongly* upcurved to a fine point, the teeth and especially the apical tooth very long, slender, and arcuate.

Length of body, ♂ 17 mm., ♀ 17 mm.; pronotum, ♂ 6.25 mm., ♀ 5.5 mm.; fore femora, ♂ 7.65 mm., ♀ 6.5 mm.; hind femora and hind tibiæ, each, ♂ 16.25 mm., ♀ 13 mm.; ovipositor, 7 mm.

1 ♂, 1 ♀. Explorations of the Upper Missouri and Yellowstone under Lt. Warren, F. V. Hayden. I also find in the U. S. National Museum from the Riley collection 1 ♂, 2 ♀, from Nebraska, the Platte River, Nebr. (McCarthy), and Ft. Riley, Kans.

By the brevity of the first and second hind tarsal joints and the slight enlargement of the fore tibiæ in the male, this species approaches the genus Phrixocnemis, but the normal development of the armature of the hind tibiæ forbids placing it there.

55. CEUTHOPHILUS NEOMEXICANUS, sp. nov.

Dark testaceous or castaneous, glabrous, broadly but gradually infuscated, especially above, on the posterior margins of all the segments, and on the anterior portion of the pronotum, which is otherwise more or less slightly mottled, beneath and on the lower portions of the sides invariably lighter and generally more nearly unicolorous. Legs testaceous, the hind femora externally with a feeble median longitudinal infuscation sometimes visible only on the distal half, where it is often diffused and accompanied by feeble slender herring-bone infuscations on either side, the hind tibial spines feebly infuscated at apex. The antennæ are not very slender and the legs short. Fore femora distinctly stouter than the middle femora, but little longer than the pronotum and less than half as long as the hind femora, the inner carina with a subapical spine, sometimes accompanied at variable distances by a smaller one. Middle femora with 1–4 spines on the front carina, most numerous in the ♀ and the subapical the largest, the hind carina similarly armed, but one spine genicular and the others as numerous in the ♂ as in the ♂. Hind femora much shorter than the body, considerably more than twice as long as the fore femora. stout, being in the ♂ less than three times as long as broad, with hardly any subapical constriction, that is, tapering almost regularly to the apex, the surface with no raised points, the outer carina pretty regularly and rather minutely denticulate in the distal half or less, exclusive of the geniculation (♂), or minutely denticulate throughout (♀), the inner carina similar to the outer, but in the ♂ more extensively denticulate than the outer, the intervening sulcus narrow. Hind tibiæ straight in both sexes, distinctly shorter than the femora, the upper surface rather broad in the ♂ and basally constricted, beneath with a longer (♂) or shorter (♀) series of median spines, besides the apical pair; spurs subopposite, the basal pair at the end of the proximal third of the tibia (♂),* about as long as the tibial depth (♂), or two to three times as long as the tibial depth (♀), set at an angle of about 50° (♂) or 30° (♀) with the tibia and divaricating as much, their tips scarcely incurved; inner middle calcaria not greatly longer than the outer, less than half as long again as the others or as the (♂) spurs, nearly as long as the first tarsal joint. Hind tarsi much less than two fifths as long as the tibia, the first joint not so long as the rest together, the second but little longer than the third and with it a little shorter than the fourth. Cerci rather slender and regularly tapering, pointed, considerably shorter (♂) or considerably longer (♀) than the hind femoral breadth. Ovipositor about two thirds as long as the hind femora, its upper margin feebly arcuate, the apical two thirds subequal, the apex slightly upturned and very acuminate, the teeth of the inner valves long, aciculate, the distal arcuate.

Length of body, ♂ 12 mm., ♀ 11.5 mm.; pronotum, ♂ 3.5 mm., ♀ 3.25 mm.; fore femora, ♂ 4 mm., ♀ 3.6 mm.; hind femora, ♂ 8.75 mm., ♀ 7.6 mm.; hind tibiæ, ♂ 8.3 mm., ♀ 7.25 mm.; ovipositor, 5.2 mm.

4 ♂, 1 ♀. Ft. Wingate, N. Mex. (Shufeldt), U. S. Nat. Mus.

The species is most nearly allied to *C. devius*, from which it differs principally in its smaller size and the armature of the femora.

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* The single ♀ I have seen has four pairs of spurs on one tibia, the basal pair at the end of the proximal fourth of the tibia, while the other tibia has but a single non-opposite pair in the middle of the tibia. It is further anomalous in the excessive length of the spurs, in contrast to the ♂.

The following species have not been seen by me.

56. CEUTHOPHILUS SCABRIPES.

Phalangopsis scabripes Hald., Proc. Acad. Nat. Sc., Philad., vi. 364 (1853); Walk., Cat. Derm. Salt. Brit. Mus., i. 116 (1869).

Rhaphidophora scabripes Scudd., Proc. Bost. Soc. Nat. Hist., viii. 7 (1861).

Ceuthophilus scabripes Scudd., Bost. Journ. Nat. Hist., vii. 436 (1862); Walk., Cat. Derm. Salt. Brit. Mus., i. 201 (1869).

I cannot find any species which corresponds sufficiently with Haldeman's description to apply this name to it. When we are better acquainted with the forms occurring in the South, west of the Alleghanies, we may be able accurately to fix it. It was described from Selma, Alabama.

57. CEUTHOPHILUS UTAHENSIS.

Ceuthophilus utahensis Thom., Proc. Dav. Acad. Nat. Sc., i. 264, pl. 36, fig. 8 (1876).

None of the species I have seen can be referred to this. It seems to resemble *C. valgus*. It comes from Mt. Nebo, Utah. (See Appendix.)

NOTE. — *Ceuthophilus cubaensis* Walk. (*Locusta Rhaphidophora cubensis* De Haan), of Cuba, is a Pherterus, according to Bolivar and Brunner, belonging to the Anostostomata.

PHRIXOCNEMIS (φριξός, κνήμη), Gen. nov.

Closely allied to Ceuthophilus, and having its general aspect, though the legs are stouter than is commonly the case in that genus. Head rather large, the vertex well rounded and deflexed, barely interrupted from continuation into the frontal costa by the confluence of the antennal scrobes. Eyes small, subpyriform, as large as the antennal scrobes. Antennæ as in Ceuthophilus. Palpi very small, the antepenultimate joint but little shorter than those on either side of it. Pronotum sub-semicylindrical, the inferior margin of the descending lateral lobes arcuate, the anterior and posterior angles equally or almost equally rounded; those of the meso- and metanotum similarly rounded without the posterior oblique truncation common in Ceuthophilus, or present in the slightest degree. Anterior coxæ compressed and elevated to form a median denticle. Legs short and rather stout. Fore femora stout, or at least broad by compression. Middle femora unarmed apically, or, when armed, only by an inferior and brief spine on the posterior side, the genicular lobes very small. Hind femora very broad and incrassate, even the extremity stout, both inferior carinæ feebly denticulate, rarely with any conspicuous spines. Fore tibiæ unarmed above, enlarged in the male; middle tibiæ armed above with several pairs of spines besides those beneath; hind tibiæ stout, no longer than hind femora, armed beneath with a single apical spine besides the apical pair and above with lateral spines of two classes: a larger series of generally long stout spines, longer than the calcaria, and, especially in the ♀, becoming longer and more crowded apically, the 4–6 spines of one row not greatly divergent from those of the other; and minute denticulations occupying the interspaces, at least on the proximal half of the tibia and the proximal free portion, but, at least in the ♀, commonly absent from the distal half of the tibia; the three pairs of apical calcaria are not widely different in length. Hind tarsi short, much less than half as long as the tibiæ, the first and fourth joints, and the second and third joints, respectively subequal, the latter together much shorter than either of the others. Ovipositor equal in breadth throughout, when viewed laterally scarcely or not tapering in the basal half.

Table of the Species of Phrixocnemis.

Hind tibiæ of male strongly bowed; distal hind tibial spurs of male as widely separated as the proximal . . . . *truculentus.*
Hind tibiæ of male straight or almost straight; distal hind tibial spurs of male much more closely approximated than the proximal.
  Nearly uniform in coloring; vertex at tip, between upper bases of antennæ, bituberculate; four pairs of hind tibial spurs in the male . . . . *validus.*
  Distinctly particolored; vertex at tip, between upper bases of antennæ, not bituberculate; five pairs of hind tibial spurs in the male . . . . *bellicosus.*

PHRIXOCNEMIS TRUCULENTUS, sp. nov.

Extreme apex of vertex with a slight depression. Body glabrous, pale luteous, becoming rufo-luteous on the dorsum, where it is heavily marked with blackish or blackish fuscous, particularly on the posterior margins of the segments, the abdominal segments almost wholly brownish fuscous with only an anterior luteous stripe, the meso- and metanotum more rufo-luteous than blackish fuscous, and the pronotum rufo-luteous above, luteous on the sides, with heavy fuscous markings, particularly an anterior bordering not reaching the lower margins and thrusting back subdorsal stripes which are broadly separated by rufo-luteous, all of which is sometimes very obscure; legs luteous, the hind femora externally tinged with rufo-fuliginous, in which fuscous scalariform markings more or less feebly appear. The antennæ are moderately slender and the legs short. Fore femora considerably stouter than the middle femora, as long as (♂) or less than a fifth longer than (♀) the pronotum, and considerably less than half as long as the hind femora, the inner carina with two or three feeble denticulations; fore tibiæ subullate, considerably stouter than the middle tibiæ. Middle femora with 1–3 short spines on the front carina, the hind carina with 4–5 very short but not very slight spines (♂) or 1–2 feeble denticulations (♀), besides a very short inferior depending genicular spine, at least in the ♀. Hind femora much shorter than the body, but considerably more than twice as long as the fore femora, stout and heavy, being in the ♂ about two and a half, in the ♀ about two and three quarters time as long as broad, with a rather strong pregenicular constriction beneath in the ♂, the upper carinate margin of the inner surface with a series of distant denticulations, the outer carina almost angularly elevated in the middle, armed, mostly beyond the middle, with a strong serration and just before the genicular lobes with a short arcuate compressed rather blunt triangular spine, serrate on its proximal edge, as long as the tibial depth, followed by a nearly similar but smaller tooth upon the genicular lobe (♂) or with a post-median spine much shorter than the shortest tibial spurs, another pregenicular spine of smaller size, and between them 6–8 spinules (♀), the inner carina with a uniform series of raised points (♂), or with small denticulations throughout, similar to these of the outer carina but with no large spines (♀), the intervening sulcus moderate. Hind tibiæ strongly and pretty regularly bowed (♂) or faintly arcuate (♀), triquetral, deeper than broad, only three fourths (♀) or a little more than three fourths (♂) the length of the hind femora, armed beneath with a single preapical spine besides the apical pair; spurs subopposite, in the ♂ four pairs in number, the basal at about the end of the proximal third of the tibia, markedly increasing in length toward the tarsi, so that the proximal are only half as long as the distal, the middle ones slightly longer than the tibial depth, set at an angle of about 70° with the tibia and divaricating about 45°; in the ♀ six pairs in number, the basal placed before the end of the proximal fourth of the tibia and just beyond a slight but distinct constriction of the tibia, the distal series as long again as the proximal, the inner series a little longer than the outer, the shortest not exceeding in length the tibial depth, the proximal more recumbent than the distal and therefore set at an angle with the tibia varying from 40° to 75°, divaricating 20°–30°, the whole faintly incurved; inner middle calcaria of ♂ scarcely longer than the others or than the distal spurs and much shorter than the first tarsal joint; calcaria of ♀ subequal but decreasing in length from above downward, those of opposite sides subequal, the longest no longer than the shortest tibial spurs and much shorter than the first tarsal joint. Hind tarsi about two fifths as long as the tibiæ, the first and fourth joints subequal, and either nearly twice as long as the second and third, which again are subequal, and all but the last apically produced beneath in the ♀ to a spinous point. Cerci slender, tapering regularly, about three fourths as long as the femoral breadth. Ovipositor short, hardly as long as the fore femora, straight, broad even at apex, the extreme upper tip of which is feebly produced; teeth of inner valves aculeate, arcuate.

Length of body, ♂ 15 mm., ♀ 16 mm.; pronotum, ♂ 5 mm., ♀ 4.5 mm.; fore femora, ♂ 5 mm., ♀ 5.25 mm.; hind femora, ♂ 12.5 mm., ♀ 11.25 mm.; hind tibiæ, ♂ 10.5 mm., ♀ 8.5 mm.; ovipositor. 5 mm.

2 ♂, 1 ♀. Peru, Nebr., Professor Townsend; Colorado, July, Snow, Coll. Univ. Kans., — all through L. Bruner.

PHRIXOCNEMIS VALIDUS, sp. nov.

Nearly uniform testaceous, glabrous, with feeble infuscation in clouds upon the sides of the pronotum, and to a scarcely perceptible degree upon the whole dorsum, made more evident by a fine mediodorsal luteous thread down the whole body, the legs of the body color, but the apical half of the femora more or less though at most feebly infuscated and the hind femora tipped narrowly with fuscous: the hind femora have also a faint rufous tinge. The antennæ are moderately stout and probably at least three times as long as the body, and the legs short and stout, the vertex rudely bituberculate. Fore femora distinctly stouter than the middle femora, a sixth longer only than the pronotum and half as long as the hind femora, the inner carina furnished with a row of minutest denticles but with no subapical spine. Middle femora with three subequal spines on the front carina, the hind carina unarmed and apparently with no genicular spine. Hind femora very much shorter than the body, twice as long as the fore femora, very stout, being not over two and a half times longer than broad, with only two or three raised points on the inner edge of the upper surface beyond the middle, the outer and inner carinæ similarly armed with minute denticulations, the intervening sulcus not broad. Hind tibiæ considerably shorter than the femora, straight, stout, armed beneath with a single small preapical spine, besides the unusually long apical pair; the four pairs of spurs are opposite or subopposite, the basal near the end of the proximal third of the tibia, regularly increasing in length distally, so that the last are as long as the nearest calcaria, while the proximal are but little more than half that length or than the tibial depth, set at an angle of 70–80° with the tibia and divaricating only about 20°, the whole feebly incurved, the tips not more so; the spurs are also more closely crowded on the distal half of the tibia than before it, and indeed so crowded as to have no intervening spines, which even between the others are few in number and irregular, the two distal spurs with the proximal calcaria being at uniform distances apart, a distance hardly one half that which separates the preceding spurs; all the calcaria are subequal in length, those of opposite sides similar, but they decrease slightly from above downwards, and the longest is as long as the first to third tarsal joints combined. Hind tarsi hardly more than a third as long as the tibiæ, the first and fourth joints subequal and either of them much longer than the subequal second and third joints combined. Cerci moderately stout, equal and single jointed in proximal half, tapering pointed and multiarticulate beyond, the whole about as long as the width of the hind femora.

Length of body, 15 mm.; antennæ, 29+ mm.; pronotum, 4.3 mm.; fore femora, 5 mm.; hind femora, 10 mm.; hind tibiæ, 9 mm.

1 ♂. California, H. Edwards.

PHRIXOCNEMIS BELLICOSUS, sp. nov.

Vertex smooth. Rather bright luteo-testaceous, subglabrous, very broadly marked with blackish fuscous especially in a broad anterior bordering to the pronotum, and a broader or narrower posterior bordering to all the segments, relatively broader on the abdominal than on the thoracic segments, but on the latter sometimes reinforced by a stout mediodorsal stripe deeper in color posteriorly than anteriorly; the interior edges of the anterior and posterior borderings of the pronotum are very irregular, and particularly show subdorsal posterior thrusts of the anterior, and laterodorsal anterior thrusts of the posterior bordering; the lower borders of the thoracic segments are broadly luteous and immaculate; the legs are luteous, the femora infuscated more or less especially beyond the middle, the hind pair with more or less distinct scalariform markings. The antennæ are slender and about three times as long as the body, and the legs short. Fore femora distinctly stouter than the middle femora, very little longer than the pronotum and much less than half as long as the fore femora, the inner carina, at least in the male, with a couple of minute subapical spines; fore tibiæ much stouter in the ♂ than in the ♀. Middle femora with two (♂) or 0–1 (♀) spines on the front carina, the hind carina quite unarmed, even wanting a genicular spine. Hind femora about two and a third times longer than the fore femora but much shorter than the body, very stout, being about two and three quarters times longer than broad (narrower in the ♀), the upper surface with 3–4 raised points on its inner edge, the outer carina in the male elevated, arcuate, with about eleven subequal small triangular spines in the distal half, in the female hardly elevated with similar but very feeble spinules, the inner carina with a series of smaller denticulations, the intervening sulcus narrow, but in the male deep. Hind tibiæ very stout, much shorter than the femora, broadly and faintly arcuate, but in the female this is scarcely perceptible, armed beneath with a single subapical spine besides the apical pair; the five (♂) or six (♀) pairs of spurs are subalternate, the basal at about the end of the proximal fourth of the tibia, increasing in length from the first to the penultimate, the ultimate and the three calcaria then decreasing in reverse order, the proximal not much more than half as long as the distal and much shorter than the tibial depth, the distal spurs more closely crowded than the proximal, and lacking between them the few and irregular spines of the second order found between the proximal, all set at an angle of 60–70° with the tibia and divaricating 20–30° only, the whole feebly incurved, their tips perhaps slightly more; calcaria of opposite sides subequal, the longest (uppermost) shorter than the first tarsal joint. Hind tarsi much less than half as long as the tibiæ, the first and fourth joints subequal and either of them more than twice as long as the subequal second and third joints together. Cerci slender and no longer than the width of the hind femora. Ovipositor slender and of uniform width excepting a slight apical expansion, about as long as the hind tibiæ, the tip acutangulate, at an angle of about 40°, slightly upturned, the inner valves crenato-denticulate with four projections which face posteriorly.

Length of body, ♂ 11.5 mm., ♀ 9.5 mm.; antennæ, ♂ 31+ mm., ♀ (est.) 18+ mm.; pronotum, ♂ 4 mm., ♀ 3 mm.; fore femora, ♂ 4.3 mm., ♀ 3.35 mm.; hind femora, ♂ 9.9 mm., ♀ 8 mm.; hind tibiæ, ♂ 8.5 mm., ♀ 6 mm.; ovipositor, 6 mm.

1 ♂, 1 ♀. Colorado, H. K. Morrison, the ♂ at an elevation of 7,000′, the ♀ at one of 5,000′ (the ♂ therefore probably in the Ute Pass, the ♀ on the plains between Denver and Colorado Springs).

DAIHINIA HALDEMAN.

Daihinia Hald., Proc. Amer. Assoc. Adv. Sc., ii. 346 (1850); Girard, Marcy Expl. Red River, 257 (1853); Scudd., Bost. Journ. Nat. Hist., vii. 443 (1862).

Not *Daihinia* Sauss., Orth. Nova Amer., i. 14–15 (1859).

This genus is remarkable for lacking the third tarsal joint of the fore and hind legs. Brunner (Monogr. Stenop., 60, foot-note) presumed this to be an abnormal condition found in a single specimen seen by me; but it was seen and specially remarked upon both by Haldeman and Girard before me, and I have examined fourteen specimens of both sexes, all of which agree in this particular except that in two or three of them the fore or hind tarsi, or both, are broken, so that it cannot be affirmed of them. There can be no question that it is normal as no specimen of the two species has been found in which the condition was different.

Table of the Species of Daihinia.

Hind femora of male about two and a half times longer than broad, armed with 3–4 very large spines on the apical half of the outer carina much larger than the others, the inner carina much more feebly armed; hind tibiæ armed beneath with a single subapical spine . . . . *brevipes.*

Hind femora of male fully three times as long as broad, the spines of the outer carina nearly uniform and much less prominent than those of the inner carina; hind tibiæ armed beneath with a row of spines . . . . *gigantea.*

DAIHINIA BREVIPES.

Phalangopsis (*Daihinia*) *brevipes* Hald.!, Proc. Amer. Assoc. Adv. Sc., ii. 346 (1850); Walk., Catal. Derm. Salt. Brit. Mus., i. 116 (1869).

Daihinia brevipes Girard, Marcy Expl. Red River, 257, pl. 15, figs. 9–13 (1853); Id., Ibid., 246, pl. 15, figs. 9–13 (1854); Scudd.!, Bost. Journ. Nat. Hist., vii. 443, fig. 3ab (1862); Walk., Catal. Derm. Salt. Brit. Mus., i. 205 (1869); Glover, Ill. N. A. Entom., Orth., pl. 7, figs. 14, 15 (1872); Brunn., Monogr. Stenop., 60 (1888); Brun., Publ. Nebr. Acad. Sc., iii. 31 (1893).

Upper waters of the Red River of Arkansas (Girard), Platte River above Ft. Laramie, Wyo. (Haldeman, Scudder); Sand Hills, Western Nebraska, and other points in Nebraska, as Sugar Cañon and Thedford, Thomas Co. (Bruner); Ft. Hays, Ellis Co., Kans., J. A. Allen (Mus. Comp. Zoöl.); Ellis, Kansas, Watson (Mus. Comp. Zoöl.); Kansas (Bruner); Black Hills, South Dakota (E. P. Austin); a specimen was also obtained during the Pacific R. R. Surveys under Lt. E. G. Beckwith, U. S. A., near Lat. 38°, presumably in Southern Colorado, and it was taken by Snow in Colorado (Bruner). The species therefore extends along the eastern margin of the Rocky Mts. from Lat. 34° to 44° N.

DAIHINIA GIGANTEA.

Daihinia gigantea Brun.!, Bull. Washb. Coll., i. 127 (1885); i. 195 (1886).

Udeopsylla gigantea Brun.!, Can. Ent., xxiii. 39 (1891); Id., Publ. Nebr. Acad. Sc., iii. 31 (1893).

Labette and Berber Cos., Kans. (Bruner). Bruner also reports it to be found in Nebraska and the Indian Territory.

NOTE. — *Daihinia mexicana* Sauss. is not a Daihinia, nor one of the Ceuthophili, but has been placed by Brunner in the genus Glaphyrosoma among the Anostostomata

UDEOPSYLLA SCUDDER.

Udeopsylla Scudd., Bost. Journ. Nat. Hist., vii. 442 (1862); Brunn., Monogr. Stenop., 59 (1888).

Table of the Species of Udeopsylla.

Body piceous, occasionally with faint rufous spots . . . . *nigra.*
Body varying in color from dark testaceous to mahogany brown. *robusta.*

UDEOPSYLLA NIGRA.

Udeopsylla nigra Scudd.!, Can. Nat., vii. 284–285 (1862); Id.!. Bost. Journ. Nat. Hist., vii. 443, fig. 2 (1862); Walk., Catal. Derm. Salt. Brit. Mus., i. 205 (1869); Thom., Rep. Geol. Geogr. Expl. Surv. 100th Mer., v. 902 (1875); Broadh., Trans. St. Louis Acad. Sc., iii. 345 (1876); Caulf., Rep. Ent. Soc. Ont., xviii. 63, 69 (1886); Brun., Bull. Washb. Coll., i. 195 (1886); Brunn., Monogr. Stenop., 60 (1888); McNeill, Psyche, vi. 27 (1891); Osb., Proc. Iowa Acad. Sc., i. ii. 119 (1892); Brun., Publ. Nebr. Acad. Sc., iii. 31 (1893); Blatchl., Proc. Ind. Acad. Sc., 1892. 153 (1894).

Ceuthophilus niger Scudd.!, Bost. Journ. Nat. Hist., vii. 437 (1862); Walk., Catal. Derm. Salt. Brit. Mus., i. 202 (1869); McNeill, Psyche, vi. 27 (1891); Blatchl., Proc. Ind. Acad. Sc., 1892, 153 (1894).

The specimens described by me as a Ceuthophilus belong to this species, though separately described at the same time.

Specimens are recorded as having been taken, or have been seen by me, from Perry Co., Ill., Dr. E. R. Boardman (Uhler); Illinois (Uhler, Comstock, McNeill); Southern Illinois and Rock Island, Ill. (Uhler); Red River, Manitoba (Caulfield); Carbery, Manitoba, in the gizzard of a sparrowhawk (Fletcher); Northern Minnesota, leaping about in the grass at midday (Scudder); Denison, Crawford Co., Iowa, July 13, 15, 20 (J. A. Allen); Iowa (Osborn); Nebraska City and the Platte Valley, Nebr. (F. V. Hayden); Nebraska City, West Point, and Pine Ridge, Nebr. (Bruner); Northeast Nebraska (Bruner); Berber Co., Kans., and Topeka, Kans., Cragin (Bruner); Missouri (Broadhead); Sedalia, Mo. (U. S. Nat. Mus.); Dakota (Bruner), and Colorado, 5,000′ (Morrison); so that its general range appears to be between the Mississippi River or a little east of the main stream to the Rocky Mountains between Lat. 37° and 50° North. But I have two specimens in my collection, one from North Carolina (Shute), the other from El Dorado Co., Calif., 4,000′ (Gissler), both of them far beyond the otherwise known limits of the species. Of the latter locality I entertain no doubt, especially as I have recently found in the Museum of Comparative Zoölogy a single specimen collected by Morrison in Arizona; but as to the former I am inclined to believe the label became accidentally attached to the wrong insect, particularly as Shute's collection was made on the seaboard.

UDEOPSYLLA ROBUSTA.

Phalangopsis (*Daihinia*) *robustus* Hald.!, Proc. Amer. Assoc. Adv. Sc., ii. 346 (1850); Walk., Catal. Derm. Salt. Brit. Mus., i. 117 (1869).

Daihinia robusta Girard. Marcy Expl. Red River, 1853, 257; 1854, 246.

Udeopsylla robusta Scudd.!, Bost. Journ. Nat. Hist., vii. 442 (1862); Walk., Catal. Derm. Salt. Brit. Mus., i. 205 (1869); Pack., Guide Ins., 565 (1869); Thom.. Proc. Acad. Nat. Sc. Philad., 1870, 77; Glov., Rep. [U. S.] Dep. Agric., 1871, 79; Thom., Ann. Rep. U. S. Geol. Surv. Terr., ii. 265 (1871), v. 437 (1872); Scudd.!, Rep. U. S. Geol. Surv. Nebr., 249 (1872); Glov., Ill. N. A. Ent., Orth., pl. 8, fig. 9 (1872); Scudd.!, Ann. Rep. Geogr. Surv. West 100th Mer., 1876, 279; Thom.. Bull. U. S. Geol. Geogr. Surv. Terr., iv. 485 (1878); Scudd.!, Rep. U. S. Ent. Comm., ii. App. 23 (1881); Brun., Bull. Washb. Coll. i. 127 (1885); Brunn., Monogr. Stenop., 59–60, fig. 31 (1888); Osb., Proc. Iowa Acad. Sc., i. ii. 119 (1892); Brun., Publ. Nebr. Acad. Sc., iii. 31 (1893).

Udeopsylla compacta Brun.!, Can. Ent., xxiii. 38–39 (1891); Id., Publ. Nebr. Acad. Sc., iii. 31 (1893).

Specimens have been seen by me from Clifford, N. Dak. (Bruner), explorations in Dakota under Gen. Sully (Rothhammer); Sheridan, Wyo. (Bruner); Ft. Fettermann, Wyo. (U. S. Nat. Mus.); above Ft. Laramie, Wyo.; Denison, Crawford Co., Iowa, July 15 (J. A. Allen); Holt Co., Pine Hills, Lincoln, and Broken Bow, Nebr. (Bruner); Nebraska City and the banks of the Platte (Hayden); Nebraska (P. R. Uhler and Miss Walker); Republican River, Nebr. or Kans. (W. T. Wood); Syracuse, Kans. (U. S. Nat. Mus.); Pacific R. R. Surveys, Lat. 38° (Lt. Beckwith); Colorado (U. S. Nat. Mus.); Albuquerque, N. Mex., Wickham (Bruner); Texas (Uhler); Pasadena, Cal. (Bruner). From the same States or Territories it has also been reported as follows: Dakota and Wyoming (Thomas); Holt and Wheeler Cos., Nebr. (Bruner), New Mexico (Bruner, Scudder), and Texas (Brunner). It has also been credited to the following: Montana, Southern Idaho, and Bloomington, Ill.—the last probably in error (Thomas); Missouri (Bruner); Bourbon Co., Kans. (Bruner); Colorado (Scudder); and "open sections of the Rocky Mt. region" (Thomas); besides Utah (Glover, Thomas).

GAMMAROTETTIX Brunner.

Gammarotettix Brunn., Monogr. Stenop., 60, 61 (1888).

GAMMAROTETTIX BILOBATUS.

Ceuthophilus bilobatus Thom.!, Ann. Rep. U. S. Geol. Surv. Terr., v. 437 (1872).

Gammarotettix californicus Brunn., Monogr. Stenop., 61, fig. 32 (1888).

California (Brunner, Behrens); Marion and Sonoma Cos., Cal. (Osten Sacken); Lakeport, Lake Co., Gilroy, Santa Clara Co., Chrystal Springs, San Mateo Co., and San Diego, Cal. (Crotch); Santa Cruz Mts., Santa Clara Co., Los Angeles Co., Cal. (U. S. Nat. Mus.).

APPENDIX.

After this paper was in type, I received from the Davenport Academy of Natural Sciences, through the kind intervention of Prof. Herbert Osborn, of Ames, Iowa, the single type of *Ceuthophilus utahensis* Thom. (see p. 102), and append a description of it to render this paper more complete. It is not so closely related to *C. valgus* as I had supposed from the description and figure, but belongs rather in the near vicinity of *C. uhleri* and *C. blatchleyi*, though with the inferior sulcus of the hind femora not so exceptionally broad as in those species, and also with very different markings, in which respect it recalls rather *C. pallidus*. The measurement of the hind tibiæ given by Thomas is too great. The specimen was collected in alcohol, but has since been pinned.

Brownish fuscous with dull luteous markings; on the pronotum the fuscous borders all the margins broadly, the anterior and lateral margins very broadly, sending backward from in front a broad mediodorsal stripe nearly meeting the posterior bordering, and through it runs a faint median luteous thread; the posterior bordering throws forward on either side a subdorsal tooth embracing the posterior end of the mediodorsal stripe and leaving between the two a U-shaped luteous mark which connects the luteous disks of either side, the latter of which are more or less mottled with fuscous lines; the meso- and metanotum are heavily spotted anteriorly with partly confluent luteous spots, and the abdominal segments are more regularly margined anteriorly with luteous; legs warm luteous, the hind femora with the usual scalariform infuscations. The antennæ are moderately slender and more than twice, probably thrice, as long as the body, and the legs moderately long. Fore femora no stouter than the middle femora, a little less than half as long as the hind femora, scarcely more than a third longer than the pronotum, the inner carina with a moderately long preapical spine preceded by a shorter one. Middle femora with a single moderately long spine on the front carina and on the hind carina 1–2 short spines besides a moderate genicular spine. Hind femora nearly as long as the body, somewhat more than twice as long as the fore femora, moderately stout, only the distal sixth subequal, about three and a quarter times as long as broad, the surface with a very few raised points along the upper edge of the inner side, the outer carina considerably and subequally elevated, with about fifteen coarse but rather small subequal and inequidistant spines, the longest not a third as long as the tibial spurs, the inner carina with a series of rather distant short spinules partially biseriate, the intervening sulcus broad, equal, and deep. Hind tibiæ rather feebly and broadly sinuate (this point is exaggerated in the original figure), a very little longer than the femora, armed beneath with a single long preapical spine besides the apical pair; spurs subalternate, the basal beyond the end of the proximal third of the tibia, nearly twice as long as the tibial depth, set at an angle of about 35° with the tibia and divaricating about 80°, their apical third or fourth considerably incurved; inner middle calcaria considerably longer than the outer, fully twice as long as the others or as the spurs, but somewhat shorter than the first tarsal joint. Hind tarsi about two fifths as long as the tibiæ, the first joint as long as the rest together, the second and fourth subequal, and each about twice as long as the third. Cerci rather stout, tapering regularly, about as long as the femoral breadth.

Length of body, 14.5 mm.; antennæ, 31+ mm.; pronotum. 4.4 mm.; fore femora, 6 mm.; hind femora, 13 mm.; hind tibiæ, 13.5 mm.

1 ♂. Mt. Nebo, Utah, August, Putnam (Dav. Acad. Nat. Sc.).

July 20, 1894.

IV.

CONTRIBUTIONS FROM THE GRAY HERBARIUM OF HARVARD UNIVERSITY, NEW SERIES, NO. VIII.

NEW PLANTS COLLECTED BY MESSRS. C. V. HARTMAN AND C. E. LLOYD UPON AN ARCHÆOLOGICAL EXPEDITION TO NORTHWESTERN MEXICO UNDER THE DIRECTION OF DR. CARL LUMHOLTZ.

By B. L. Robinson and M. L. Fernald.

Presented May 9, 1894

Crossosoma parviflora. A shrub, 4–8 feet high: branches covered with gray bark; branchlets slender, elongated, and often flexuous, sometimes straight and a little rigid; cortex yellow: leaves elliptic-oblong, obtuse and mucronulate at the apex, pale green upon both surfaces, thickish, 1-nerved, 4–6 lines long, 1½–2¼ lines broad: sepals 5, broadly oblong or suborbicular, 1¾–2¼ lines long: petals 5, oblong, 3 lines in length: stamens 15–20: carpels 3–4; follicles glabrous, reticulated, only 3–3½ lines long. — Collected in the Grand Cañon of the Colorado, by Dr. Gray, February to May, 1885, but referred to *Glossopetalon Nevadense*, Gray; and at La Tinaja, Sonora, at 3,700 feet, by Mr. Hartman, 19 November, 1890 (no. 245).

Eriodendron acuminatum, Wats. (Proc. Am. Acad. xxi. 418). Specimens apparently of this species, but representing other stages than those shown by the type, were collected in Western Chihuahua but without more exact locality. The older branches are armed with stout spreading spines 3–4 lines in length, while the younger ones, as Dr. Watson states, are unarmed; the young shoots and leaves are densely tomentose: the calyx deeply campanulate, an inch long, shallowly 5-toothed, glabrous and glaucous upon the outer surface, densely sordid tomentose within; teeth rounded, often split (perhaps in drying): petals linear, 5 inches long, 4 lines broad, very appressed silky upon one side of the outer surface, tomentose upon the side covered in the bud; glabrate upon the inner surface: stamens included. — The Mexican name is "Pochate." The fleshy white roots are eaten, the fine cotton is used for making wicks for tapers of wild beeswax. This species is to be distinguished from *E. tomentosum*, Robinson, by its glabrous calyx and relatively broader leaflets.

Esenbeckia Hartmanii. A shrub, 6–10 feet high: twigs thick, woody, covered with gray bark, leafy chiefly near the end: leaves simple, alternate, oblong or somewhat obovate, entire, rounded or retuse at the apex, somewhat narrowed below to an obtuse or rounded base, thickish, green, nearly smooth and finely reticulated above, tomentulose and scarcely paler beneath; the largest ones 16–20 lines long, 8–11 lines broad; the others considerably smaller (8–9 lines in length); petioles short, soft pubescent, 1–1½ lines long: inflorescences short, terminal upon the branchlets; fruiting pedicels 1–3 together, ½ inch or less in length: the capsule tuberculately roughened, 9–10 lines in diameter; pericarp white, thin and chartaceous, rather irregularly ruptured upon dehiscence; seeds subglobose, smooth, black, 3½ lines in diameter; scar white, narrow, linear, ½ line in breadth. — Collected in fruit at La Tinaja, Sonora, at 3,700 feet, by Mr. Hartman, 19 November, 1890 (no. 240). This species much resembles the Lower Californian *E. flava*, Brandegee, but differs in its smaller greener shorter-petioled leaves, and its smaller fruit with chartaceous and not cartilaginous pericarp. The seeds of *E. flava* also are larger and have a much broader scar.

Ilex rubra, Wats. (Proc. Am. Acad. xxi. 422). Flowering specimens of this species, which was originally described in fruit, have been collected in an arroyo near Coloradas, by Mr. Hartman, May, 1893 (no. 513), and add the following characters: flowers numerous, in small aggregated thyrses, greenish white, 4-parted: calyx lobes ovate, obtuse, ¾ line long: corolla nearly 4 lines in diameter, about equalling the stamens; the lobes rounded.

Dalea Lumholtzii. Stems many, slender, puberulent, punctate with yellow glands, simple or sparingly branched, erect from a decumbent much branched suffrutescent base: upper leaves erect or ascending, 1–1¾ inches long, leaflets 17–27, linear, 2–2½ lines long, nearly ½ line in breadth, obtuse, slightly narrowed to very short petiolules, glabrous, glaucous and glandular-punctate upon both surfaces; the basal leaves numerous, shorter, and with considerably smaller almost filiform leaflets, silky under a lens: spikes ovate, capitate, 3–7 lines in length, becoming oblong, very densely flowered, covered with closely imbricated persistent bracts; the latter ovate or obovate, very abruptly pointed, silky upon the margins and especially near the somewhat narrowed base; glabrate and glandular-punctate upon the back, 1½ lines long: calyx striate, sparingly silky, entirely obscured by the bracts: petals white or nearly so, oblong, obtuse, attenuate below to slender claws: stamens 10. — Collected at Las Pinitos, Sonora, at 6,100 feet, by Mr. Hartman, 14 October, 1890 (no. 133). A species with the habit of a *Petalostemon* rather than a *Dalea;* the fresh leaves very aromatic when crushed.

SEDUM LUMHOLTZII. Hoary puberulent: roots fibrous: stems herbaceous, decumbent, 5–10 inches high, ancipital, simple below the spreading cymose inflorescences: leaves soft pubescent and ciliated; the basal ones crowded, spatulate, 4–6 lines long; the cauline spatulate-oblong, obtuse, somewhat narrowed to a slightly extended base, about an inch in length, 2–3 lines broad: flowers numerous, pedicellate, white: sepals lance-oblong, obtusish, 1½ lines long, not at all extended at the base: petals lanceolate, acute, 2½ lines long: carpels 5, pruinose, erect, attenuate; styles persistent; scales small, truncate, bright red; seeds oblong, ¼ line in length. — Collected at Nacory, Sonora, at 3,700 feet, by Mr. Hartman, 4 December, 1890 (no. 287); and at Huchuerachi, Sonora, by Mr. Lloyd, 8 December, 1890 (no. 389).

SICYOS COLLINUS. Stem slender, glabrous, furrowed: tendrils 2–3-parted: leaves thin, 5-lobed, scarcely paler beneath, 1½–2½ inches long, usually narrower, roughened upon both surfaces with minute whitish tubercular hairs; lobes ovate to lanceolate, acute or acuminate, sharply dentate or denticulate; the terminal ones often elongated; petioles 4–12 lines long: ♂ peduncles 1¼–3 inches in length, smooth or nearly so; inflorescences slender, usually simple, slightly puberulent or quite smooth, ½–1½ inches long, 10–35-flowered; pedicels very slender, spreading, smooth, equal, slightly thickened at the apex, 1¾–2 lines in length: calyx teeth very minute or obsolete: corolla rotate-campanulate, 2½–3 lines in diameter, finely granular; lobes broadly ovate, obtusish: stamineal column (including the anthers) ¾ line long: ♀ peduncles 2 lines long, smooth; fruits 2–5 in a head, ovate, acuminate, compressed, nearly 3 lines long, sparingly setose, otherwise nearly glabrous; setæ 1½ lines long. — Collected on hills near Chihuahua, by Mr. C. G. Pringle, 23 October, 1885 (no. 568); and in the Cañon de San Diego, Chihuahua, by Mr. Hartman, 17 September, 1891 (no. 773). A species near *S. Deppei*, Don, but with leaves smaller and somewhat more acutely lobed; peduncles and inflorescences nearly or quite glabrous; petioles and pedicels shorter; and male flowers a little smaller.

GALIUM WRIGHTII, Gray, var. LATIFOLIUM. Pubescent below as in the type, but the branches nearly smooth: leaves elliptic-oblong, ½ inch long, 2 lines broad: fruit hispid, but the bristles fewer and shorter. — Collected on the Sierra de las Gronillas, Sonora, at 5,800 feet, by Mr. Hartman, 2 October, 1890 (no. 58); the same thing seems to have been collected by Prof. Lemmon near Fort Huachuca, S. Arizona, 1883. Some of Mr. Hartman's specimens show a tendency to intergrade with the type.

Bellis orthopoda. Perennial: rootstock short, thick, erect, giving off several tough fibres: stems 1–5, decumbent or suberect, 4–5 inches high, simple, monocephalous, appressed pubescent, very leafy to above the middle: leaves thick, entire, appressed pubescent; the radical ones numerous, spatulate, obtuse, 9 lines long, 1½–2 lines broad; the cauline linear-oblong, erect, ciliate, becoming gradually smaller and acutish: peduncles 1–1¾ inches long, appressed cinereous pubescent: heads rather large for the genus, a little over an inch in breadth; involucral bracts lanceolate, acuminate, cinereous pubescent upon the membranaceous margin, 2½–3 lines long: rays about 30, light blue in a dried state, 6 lines long. — Collected at Guachachic, Chihuahua, by Mr. Hartman, 25 June, 1892 (no. 523). This species resembles closely the low and coarse forms of *B. integrifolia,* Michx., but is to be distinguished by its vertical perennial caudex and few simple stems.

Aster lepidopodus. Perennial: root a cluster of simple fibres: stems several, slender, a foot high, scaly upon their spreading distinctly decumbent bases, hirsute, simple or bearing several erect slender nearly naked monocephalous branches: reduced basal leaves narrowly deltoid, acute, entire, scarious, glabrate except upon the ciliated margins; foliar leaves of the stem oblong-linear, acutish, entire, erect, nearly an inch in length, 1½ lines broad, glabrous, except upon the strongly ciliated margin and occasionally upon the midrib: heads about an inch in diameter; scales of the involucre 2(–3)-seriate, subequal, linear-lanceolate, acuminate; the dark herbaceous middle portion hirsute: rays 20–25, narrow, pale rose-colored: achenes columnar, hirsute, 4-ribbed. — Collected in pine forests about Chuchuichupa, Chihuahua, by Mr. Hartman, 14 June, 1891 (no. 697). A species apparently of the § *Megalastrum* as regards involucre and achene, but more slender and less rigid in habit than the other species of this group.

Franseria nivea. Finely white tomentose or pale cinereous throughout, 1–4 feet high: pubescence persistent except upon the base of the stem: leaves alternate, 2 inches long, somewhat broader, 3-parted to the base; parts deeply pinnately lobed; segments acutish, toothed;

petioles 1¼–1½ inches long, often somewhat winged or lobed near the summit: terminal inflorescences about 2 inches long, rather closely flowered, staminate, except at the very base; inflorescences springing from the upper axils several, very short, chiefly fertile; ♂ pedicels flexuous, 2 lines long, white tomentose and not at all glandular; involucres cinereous, rotate, 2 lines in diameter, unequally 9–10-toothed, 20-flowered; teeth obtuse; ♀ involucres at first ovoid, acute, 2-beaked, 2-celled; spines (scales) about 24, appressed, imbricated; achenes solitary in each cell; fruit 2½ lines long, puberulent and finely glandular, corrugated toward the narrowed base; the spines spreading, ⅔ line long. — Collected on plains near Casas Grandes, Chihuahua, by Mr. Hartman, 10 October, 1891 (no. 813).

ENCELIA OBLONGA. Fruticose, 2–3 feet high: branches grayish, nearly or quite smooth, finely striated; branchlets glabrous or hirsute, resiniferous: leaves attenuate, subsessile, oblong or oblanceolate, puberulent, green upon both surfaces, scabrously ciliolate-denticulate, rounded or obtuse and mucronate at the apex, cuneate at the base, 1¼–2½ inches long, 6–12 lines broad; veinlets translucent: peduncles solitary, terminal, sparingly hirsute, 2–3 inches in length, with 2–3 reduced leafy bracts and a solitary head about an inch in diameter exclusive of the rays: involucral bracts in two series, subequal, lanceolate, caudate-attenuate, ciliolate, 5–6 lines long: rays 12–15, yellow, nearly half an inch in length: disk corollas with throat cylindrical, 2 lines long, much exceeding the short proper tube and still shorter glabrous limb: achenes 2½ lines long, appressed silky villous and crowned with two weak unequal readily deciduous ciliolated awns; the larger one, on the side opposite the enclosing palea, two thirds as long as the corolla. — Collected on plains near Casas Grandes, Chihuahua, by Mr. Hartman, 10 October, 1891 (no. 812).

LEPTOSYNE ARIZONICA, Gray, var. PUBESCENS. Soft pubescent throughout: leaves tending to have somewhat broader segments: not otherwise differing from the glabrous type. — Collected at Granados, Sonora, at 2,950 feet, by Mr. Hartman, 15 November, 1890 (no. 222); near Huchuerachi, at 4,000 feet, by the same collector, 5 December, 1890 (no. 296); and at Cardovas, Sonora, by Mr. Lloyd, 9 December, 1890 (no. 406).

PERITYLE LLOYDII. Suffruticose, branching from the base, 4–10 inches high, cinereous-pubescent, very glandular and aromatic: branches slender, terete, more or less decumbent: leaves opposite below, subalternate above, ovate-deltoid, acute, somewhat doubly dentate, 8–12 lines long, pubescent upon both surfaces; petioles slender, 5–9 lines in length: peduncles springing from the upper axils, about 2 inches long, slightly thickened upward: heads large, radiate, 5 lines high, including the rays 9 lines broad; scales of the involucre narrowly linear, ⅓ line wide, caudate-attenuate, 4 lines in length: ray flowers 18–20, pale yellow; ligules 3 lines long, 3-toothed at the apex: disk flowers including achenes 4½ lines long: style branches of the latter with attenuate hispid appendages, those of the former smooth: achenes oblong, black with thickened white margins, puberulent, scarcely ciliolate, 1½ lines long. — Collected in niches of dry rocks at Badehuache, Sonora, by Mr. Lloyd, 2 December, 1890 (no. 400). A species nearly related to *P. leptoglossa*, Gray, and *P. Palmeri*, Wats.; distinguished from the former by its much more copious pubescence, more attenuate involucral scales, and larger flowers; from the latter by its slender terete branches, and by its achenes which are scarcely ciliolate instead of having a copious ciliation.

CACALIA GLOBOSA. Caudex short, horizontal, giving off numerous fibres: stem simple, flexuous, 8 inches in height, glabrate, except near the somewhat fuscous-tomentose summit: leaves thickish, nearly or quite glabrous, somewhat glaucous, cartilaginous upon the crenate-dentate margins, obtuse, pinnately veined; the radical ones deltoid, 1¼ inches long, nearly as broad, cordate with a broad shallow sinus; their petioles 1½ inches long, slender above, dilated below; the cauline leaves for the most part consisting of ovate clasping cartilaginous dentate phyllodia; only the lower ones surmounted by an ovate or deltoid crenate blade: heads about 6-flowered, densely packed together in a globular inflorescence (9 lines in diameter): involucral scales obovate-oblong, 3 lines in length, with ciliate margins and tip, thickened in the middle, especially near the summit: corollas 2¼ lines high; the linear lobes little exceeding the tube: pappus sparing. — Collected in a moist meadow, Guachuchic, Chihuahua, by Mr. Hartman, 25 June, 1892 (no. 522).

PHILIBERTIA CYNANCHOIDES, Decsne., var. SUBTRUNCATA. Leaves narrow, attenuate, abrupt at the base or subcordate with a very shallow open sinus and spreading auricles. — Collected at Fronteras, Sonora, at 4,550 feet, by Mr. Hartman, 25 September, 1890 (no. 4). The type both by description and authenticated specimens has deeply cordate and usually broader leaves. No other differences have been noted.

PHACELIA RUPICOLA. Perennial, hirsute, subacaulescent: leaves springing from an elongated thickish ascending caudex, deeply pinnatifid; blade oblong in outline, 2–3 inches long, equalling the petiole; segments 15–19, broadly oblong, acutish, generally 1–2-toothed upon the lower margin, 5–7 lines long, 2½–4 lines broad; the upper ones approximate; the lower becoming smaller and more or less scattered: inflorescence exceeded by the leaves, loose below, the lowest pedicels being 1½ inches long: calyx lobes oblong-lanceolate, acute, slightly unequal, 2–3½ lines long: corolla pure white, ½ inch in diameter; lobes rounded, cleft half-way to the base; appendages linear, folds free at the tip and forming pairs alternating with the stamens: filaments equalling the corolla, hirsute below: style 2-parted for two thirds of its length and easily divided to the base; ovary hirsute; ovules about 20. — Collected on cliffs in a pine forest of Strawberry Valley, Chihuahua, by Mr. Hartman, 8 June, 1891 (no. 686). A species of the § *Eutoca*.

LYCIUM RETUSUM. Stems glabrous, smooth, dark brown or grayish, sometimes armed with short slender spines; branchlets divaricate: pulvini white, pubescent; leaves obovate, cuneate, usually retuse, pubescent upon both surfaces: pedicels filiform, glandular-pubescent, 3–5 lines long: calyx tubular, glandular-pubescent, 2½ lines long; teeth triangular-lanceolate, erect, acute, a third as long as the tube: corolla trumpet-shaped, about 4 lines in length; teeth short, retuse, a fourth as long as the tube: style and stamens exserted; the latter unequal; filaments bearded at the base: fruit not seen. — Collected at Opata, Sonora, at 3,450 feet, by Mr. Hartman, 1 November, 1890 (no. 212).

MAURANDIA (?) GENICULATA. Densely glandular pubescent and viscid: stems zigzag: leaves distichous, orbicular, cordate, coarsely crenate, 1–2 inches broad, green upon both sides, 5-nerved; petioles spreading, 5–9 lines long: peduncles axillary, ½–1 inch in length, ascending in anthesis, somewhat thickened and recurved in fruit: calyx narrowly campanulate, subequally 5-cleft to near the middle, 6 lines long; segments narrowly ovate, obtusish, 1-nerved, somewhat plaited at the sinuses: style simple, filiform, nearly or quite an inch in length; ovary superior, 2-celled; ovules numerous, upon axial placentæ: fruit capsular, about equalling the calyx; seeds oblong, barely a line in length, two thirds as thick, black, irregularly roughened with relatively large tubercles but not at all winged: corolla and stamens not seen. — Collected on cliffs at Nacory, Sonora, at 3,750 feet, by Mr. Hartman, 1 December, 1890 (no. 272). Closely resembling in foliage and pubescence *M. erecta*, Hemsl., but with a very geniculate stem and wingless seeds. Until the corolla and stamens are discovered the generic position must remain somewhat doubtful.

MIMULUS DENTILOBUS. Very pubescent or glabrate: stems slender, weak, loosely matted, decumbent, much branched, rooting at the joints, 3–6 inches in length: leaves small, suborbicular, broader than long, shallowly sinuate-dentate, cartilaginous margined; the largest 3 lines in diameter, abruptly contracted into a short winged petiole: pedicels axillary, opposite, filiform, 9–12 lines long: calyx in anthesis 2½ lines in length, slightly accrescent and loosely surrounding the fruit: corolla yellow, spotted with purple; lobes fringe-toothed; the median lobe of the lower lip somewhat retuse: anther cells not confluent: capsule compressed, obtusish, 1¼ lines in length. — Collected at Nacory, Sonora, at 3,750 feet, by Mr. Hartman, 4 December, 1890 (no. 288); and on the Bavispe River, Sonora, by Mr. Lloyd, 23 December, 1890 (no. 440). Habit of *M. Madrensis*, Seem., but with fringed corolla.

SALVIA RUBROPUNCTATA. Suffrutescent: stems branched, grayish; branches brown, slightly scabrous, pulverulent: leaves ovate-oblong, obtuse or rounded at the apex, abruptly contracted to a cuneate base, finely crenate-serrate, punctate with dark red dots, at first strongly rugose above and white-tomentose beneath, becoming nearly smooth and glabrous; the largest 1½ inches long, half as broad; many smaller ones clustered in their axils: spikes subcapitate, terminal, solitary, or 2–3 together, short-peduncled; floral leaves lanceolate, slightly exceeding the calyx; verticels about 6-flowered, approximate: calyx 2½ lines long, covered with dense bluish wool, obscuring numerous bright scarlet glandular dots; the upper lip shortly 3-toothed; teeth acuminate: corolla blue, 6 lines in length, punctate with red glands; the lower lip about equalling the tube; the upper lanate on the outer surface. — Collected in the Cañon Huehuerachi, Sonora, by Mr. Lloyd, 12 December, 1890 (no. 451). The species appears to belong to § *Erianthæ*. It is noteworthy for the bright red glands which cover all parts of the flower, but are nearly or quite hidden by the enveloping bluish wool.

ARCEUTHOBIUM sp. Staminate plant very robust, 6–7 inches long, profusely branched: stem terete at the base, 5–6 lines in diameter, sheaths short, campanulate, truncate; branches more or less sharply quadrangular, bright yellow: spikes very numerous, short, few-flowered: flowers 3–4-parted; segments obtuse, ovate-oblong, arched over the stamens; the latter inserted near the middle of the segments. — Collected on pines at Pine Ridge Pass, Sonora, at 3,200 feet, by Mr. Hartman, 17 December, 1890 (no. 340). This interesting plant may be the staminate form of *A. robustum*, Engelm., or of *A. campylopodium*, var. (?) β, Engelm. From the specimens of both species at hand the present plant differs in its considerably greater size. These species, however, are too poorly known, especially in the staminate forms, to permit satisfactory determination in this case.

FICUS JALISCANA, **Wats.** (Proc. Am. Acad. xxvi. 150). Additional material of this species, collected at Granados, Sonora, at 3,700 feet, by Mr. Hartman, 15 November, 1890 (no. 217), shows that the plant has leaves often 6 inches long; also fascicled aerial roots a foot and a half (or more) in length.

SPIRANTHES VELATA. Roots clustered, tuber-like: leaves (at least at the time of flowering) none: stems 1–2, erect, 9–12 inches high, thickish and enveloped in loose white scarious brownish-veined ovate-oblong attenuate bracts; the floral bracts similar, smaller but exceeding the flowers: spike dense, oblong, 2–3 inches in length: sepals subscarious; the lateral ones oblong-lanceolate or linear-lanceolate, acuminate, 3-nerved, 4 lines long; the upper one free nearly half its length, attenuate: petals acutish, narrowly ovate, nearly as long as the upper sepal, also subscarious and brownish nerved; lip rhombic, rounded at the tip, crenulate throughout, thickish, about 6 lines long, finely granulated above and bearing two small oblong hoary-pubescent callosities at the base. — Collected in a cañon parallel with the Cañon de los Alamos on Rio San Miguel, Chihuahua, by Mr. Hartman, 28 June, 1891 (no. 710).

BRAVOA DENSIFLORA. Root of many spreading thickened fibres; bulbs loose, oblong, becoming 2 inches long and an inch or more in thickness: radical leaves linear, attenuate, 3–4 inches long, a line wide; the cauline reduced to bracts, 1–2 inches long, with broad scarious and attenuate tips; the floral similar: spike short, dense: flowers single in each bract, slender, tubular, spreading, curved, 17–22 lines long, dull yellow in a dried state, pulverulent-tomentulose upon the outer surface; limb oblique; segments ovate, obtuse, only 1–1½ lines long, erect, bearing a tuft of short white hairs at the tip: anthers inserted high up in the scarcely ampliate throat: fruit (immature) ovate, over 3 lines in diameter. — Collected on dry mesas near Varogachic, Chihuahua, by Mr. Hartman, 5 July, 1892 (no. 536).

PINUS LUMHOLTZII. A tree, 30–40 feet in height: branchlets elongated, ¼ inch in diameter: leaves in 3's, springing from the lower surface of the branchlets, pendulous, 10–13 inches long, ¾ line in breadth, nearly flat and shining upon the dorsal surface, carinate upon the ventral; margins scarcely involute: sheaths quite obsolete: bud scales lanceolate, attenuate, tawny, somewhat lacerate-ciliate, 3½ lines long: aments and cones unknown. — Collected near Coloradas, by Mr. Hartman, May, 1893 (no. 541). A beautiful species, striking in habit on account of its dense pendulous foliage, and figured in Scribner's Magazine, xvi. 38.

Marsilia mollis. Closely tufted, densely villous and cinereous throughout; hairs fine, silky, persistent or very tardily deciduous, finely warted under a compound microscope: internodes and stems in the numerous specimens at hand (terrestrial form) not at all developed: root a cluster of delicate fibres: petioles filiform, reddish brown, flexuous, 8–12 lines long, commonly nodding at the apex; leaflets deltoid-obovate, entire, rounded at the apex, broadly cuneate at the base, 1½ lines in length, equally broad: peduncles borne singly but in great numbers and closely crowded, 2½–3 lines long; conceptacles horizontal, broadly oblong, compressed, 1¾ lines long, 1¼ lines broad, densely white-villous, dull brown on the removal of the pubescence, finely 8–9-wrinkled upon each surface, or smooth, often punctate; rhaphe ½ line in length; basal teeth very obscure; sori 16–18. — Collected at San Diego, Chihuahua, at 6,000 feet, by Mr. Hartman, 20 April, 1891 (no. 604). A very small and remarkably pubescent almost lanate species.

V.

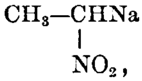
CONTRIBUTIONS FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.

ON THE CONSTITUTION OF THE NITROPARAFFINE SALTS.

BY J. U. NEF.

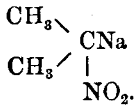
Presented May 9, 1894.

VICTOR MEYER, who discovered the nitro fatty compounds, has, as is well known, shown that the primary and secondary nitroparaffines differ from the corresponding tertiary derivatives, as well as from the aromatic nitro bodies, especially in the fact that they possess acid properties. He has explained this very noteworthy character by the assumption that the introduction of the nitro group exerts an "acid making" influence on the molecule, which, however, extends only to hydrogen atoms bound to the same carbon atom as the negative radical. He therefore supposes * sodic nitroethane to possess the constitution represented by the formula



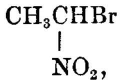
$$\begin{array}{l} CH_3\text{—}CHNa \\ \qquad\quad | \\ \qquad\quad NO_2, \end{array}$$

and, in an analogous manner, he represents the sodium salt of secondary nitropropane by the formula



$$\begin{array}{ll} CH_3\diagdown & \\ & CNa \\ CH_3\diagup & \;| \\ & NO_2. \end{array}$$

The fact that these salts, when treated with bromine, are converted into bromnitroethane,



$$\begin{array}{l} CH_3CHBr \\ \qquad\;| \\ \qquad NO_2, \end{array}$$

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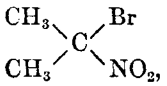
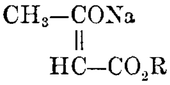
* Ann. Chem. (Liebig), CLXXI. 28, 48.

a strong acid, and into bromnitropropane,

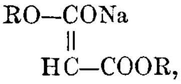


a neutral body, seems at first to be an argument in favor of this hypothesis. I have, however, already pointed out * that one is not justified in drawing from this reaction such a conclusion with regard to the nature of the sodium salts, and have further demonstrated † that the hypothesis of the acid making influence of negative groups or radicals has absolutely no justification, and is entirely illogical. That this hypothesis is no longer tenable in many cases where it has hitherto been accepted is clear. That the sodium salts of acetoacetic ether and of malonic ether possess a structure which must be represented by the formulæ



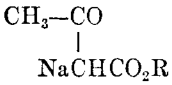
$$\begin{array}{l} CH_3\text{—}CONa \\ \quad\ \| \\ \quad HC\text{—}CO_2R \end{array}$$

and



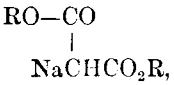
$$\begin{array}{l} RO\text{—}CONa \\ \quad\ \| \\ \quad HC\text{—}COOR, \end{array}$$

and not, as previously supposed, by the formulæ



$$\begin{array}{l} CH_3\text{—}CO \\ \quad\ | \\ \quad NaCHCO_2R \end{array}$$

and



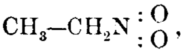
$$\begin{array}{l} RO\text{—}CO \\ \quad\ | \\ \quad NaCHCO_2R, \end{array}$$

can now be regarded as settled experimentally beyond a doubt.‡

For these reasons it is almost self-evident that the metal in the nitroparaffine salts cannot be bound directly to carbon, and is in all probability bound to oxygen; and the following experiments prove this in a most satisfactory manner.

I. Decomposition of Primary and Secondary Nitroparaffine Salts by means of Acids.

Assuming that nitroethane possesses the constitution



$$CH_3\text{—}CH_2N\begin{matrix}:O\\:O\end{matrix},$$

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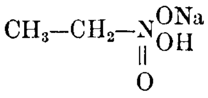
* Amer. Chem. Journal, XIII. 427.

† These Proceedings, XXVII. 157.

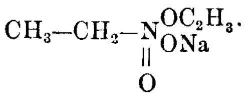
‡ Ann. Chem. (Liebig), CCLVIII. 261, CCLXVI. 52, CCLXXVI. 200, and CCLXXVII. 59.

it is very well possible * that on treating it with sodic hydrate or with sodium ethylate, an addition of these reagents to the nitro group takes place, forming thus the products,



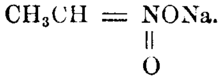
$$CH_3{-}CH_2{-}\underset{\underset{\displaystyle O}{\|}}{N}\begin{matrix}ONa\\OH\end{matrix}$$

and



$$CH_3{-}CH_2{-}\underset{\underset{\displaystyle O}{\|}}{N}\begin{matrix}OC_2H_3\\ONa\end{matrix}.$$

which by loss of water or alcohol must give sodic nitroethane of the constitution



$$CH_3CH = \underset{\underset{\displaystyle O}{\|}}{N}ONa.$$

This reaction is entirely analogous to the formation of sodic malonic ether from malonic ether and sodium ethylate,† the only difference being in the fact that sodic malonic ether is instantly decomposed by water, regenerating the ester and forming sodic hydrate,‡ whereas sodic nitroethane dissolves in water without decomposition.

In favor of this interpretation of salt formation can be adduced the fact that many higher members of the nitroparaffine series, which ought, like nitroethane, to possess acid properties, dissolve only with great difficulty and on prolonged treatment in very concentrated sodic hydrate; § i. e. they possess very weak acid properties and were consequently long considered to be neutral substances, ‖ — a fact which, as V. Meyer also observes,¶ is very noteworthy. If, however, the salt formation depends on the addition of sodic hydrate to the nitro group and subsequent loss of water, the peculiar and unexpected behavior observed in these cases is easily comprehensible; the first members of the nitroparaffine series are soluble in water, and thus more easily attacked by sodic hydrate, whereas the higher members are insoluble in water.

Since, according to this conception of the nitroparaffine salts, they do not possess a constitution analogous to that of the free nitro compounds, it does not of necessity follow, especially since the salts are soluble without decomposition in water, that these salts can be con-

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* These Proceedings, XXVII. 150–158.

† Ann. Chem. (Liebig), CCLXVI. 67, CCLXXVI. 244.

‡ Ibid., CCLXVI. 113.

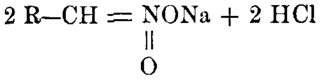
§ Ibid., CLXXV. 135, 144; Züblin, Ber. d. chem. Ges., X. 2083; Konowalow, Ber. d. chem. Ges., XXV. Ref. 108.

‖ Ber. d. chem. Ges., V. 203; Ann. Chem. (Liebig), CLXXI. 44.

¶ Lehrbuch, p. 205.

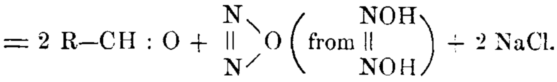
verted back again completely into the free nitro bodies from which they were obtained. The first problem therefore was to determine this point by experiment, and it was found that under no condition is it possible to convert these salts back again completely into the corresponding free nitro compounds. On adding an aqueous solution of a sodium salt of a nitroparaffine to cold dilute sulphuric or hydrochloric acid, not a trace of the nitroalkyle is regenerated, but a more or less smooth decomposition into nitrous oxide and an aldehyde or ketone takes place, according to one of the following equations:

I.



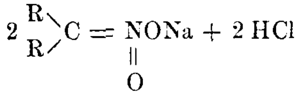
$$2\,R{-}CH = \underset{\underset{O}{\|}}{N}ONa + 2\,HCl$$

Sodium Salt of a Primary Nitroparaffine.



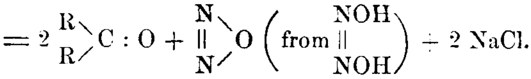
$$= 2\,R{-}CH : O + \begin{matrix} N \\ \| \\ N \end{matrix}\!\!>\!O \left(\text{from} \begin{matrix} NOH \\ \| \\ NOH \end{matrix} \right) + 2\,NaCl.$$

II.



$$2\,\begin{matrix} R \\ R \end{matrix}\!\!>\!C = \underset{\underset{O}{\|}}{N}ONa + 2\,HCl$$

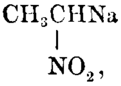
Sodium Salt of a Secondary Nitroparaffine.



$$= 2\,\begin{matrix} R \\ R \end{matrix}\!\!>\!C : O + \begin{matrix} N \\ \| \\ N \end{matrix}\!\!>\!O \left(\text{from} \begin{matrix} NOH \\ \| \\ NOH \end{matrix} \right) + 2\,NaCl.$$

This new very noteworthy decomposition of nitroparaffine salts, which always takes place, no matter how the experiment is carried out, has been overlooked by V. Meyer and by all who have worked with these compounds. V. Meyer states repeatedly that it is possible to regenerate the free nitroparaffine from its sodium salt or from a caustic alkaline solution, — a fact which is only true to a limited extent (see below). Decomposition always takes place according to one or the other of the above equations, and this fact alone proves that the nitroparaffine salts cannot possibly have a constitution analogous to that of the free nitroalkyles.

If, for example, sodic nitroethane possessed the constitution



$$CH_3\underset{\underset{NO_2}{|}}{C}HNa,$$

it ought to be possible to convert it quantitatively into $CH_3{-}CH_2NO_2$ by addition to dilute sulphuric acid, just as sodium acetate goes over completely into acetic acid on similar treatment. As a matter of fact, not a trace of nitroethane is formed.

Decomposition of Sodic Nitroethane by Acids. — Sodic nitroethane can be obtained from nitroethane by treating it in absolute ethereal solution with sodium wire, or by means of alcoholic sodic hydrate, according to the method of V. Meyer.* It is, however, best formed by addition of an alcoholic solution of sodic ethylate to an alcoholic solution of nitroethane. The salt is filtered off, well washed with alcohol, and dried on clay plates and over sulphuric acid in a vacuum; 30 grams nitroethane gave regularly 33 grams sodium salt. A complete analysis of the salt is not possible, because it explodes on heating with cupric oxide.

0.3035 gram substance gave 0.2225 gram Na_2SO_4.

	Theory for $C_2H_4NO_2Na$.	Found.
Na	23.71	23.74

On adding quickly an aqueous solution of sodic nitroethane (1 part to 10 parts H_2O) to cold dilute sulphuric acid (1 : 5), using for one gram salt about 15 to 20 c.cm. of the acid, decomposition takes place into nitrous oxide and acetaldehyde; the reaction takes place with much evolution of heat, the solution becomes colored green, and not a trace of nitroethane is regenerated. The experiment can be carried out quantitatively as follows: 15 to 20 c.cm. of dilute sulphuric acid are brought into a small distilling flask which is provided with a separatory funnel, and is connected on the one hand with a carbonic acid generator, and on the other with a Schiff's nitrometer. Air is first expelled from the apparatus by means of carbon dioxide (passed over heated copper), and then the aqueous solution of sodic nitroethane is quickly added by means of the separatory funnel and well washed down with water. The distilling flask is then heated to boiling and the nitrous oxide driven over, by a current of carbonic acid, into the azotometer. The aldehyde which is formed is absorbed by the caustic potash solution (1 : 2) in the nitrometer, which was saturated previous to the experiment with nitrous oxide.

0.7 gram substance gave 77 c.cm. N_2O at 15° and 754 mm., corresponding to 89.4% of the theoretical amount.

1.0 gram substance gave 105 c.cm. N_2O at 16° and 748 mm., corresponding to 84.6% of the theoretical amount.

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* Ann. Chem (Liebig), CLXXI. 29.

That nitrous oxide was present was shown by its characteristic reactions, and by passing a known volume of the gas over heated copper, whereby an equal volume of nitrogen was obtained.

In order to determine the amount of acetaldehyde quantitatively, the same apparatus is used except that the distilling flask, instead of being connected with an azotometer, is connected with a condenser and a well cooled receiver containing water. About one half of the solution in the distilling flask is then boiled off, and the distillate in the receiver is treated with powdered calcic carbonate to remove traces of acetic acid, and then again distilled over. The second distillate thus obtained is perfectly neutral to test paper, and is heated for four hours in a sealed tube at 100° with an excess of silver oxide.* The silver acetate formed is boiled out with water, and the amount determined by evaporating the aqueous solution.

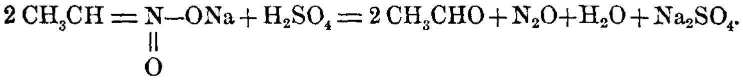
1.5 grams sodic nitroethane gave 1.8 grams silver acetate, or 69.7% of the theoretical amount.

A portion of the silver acetate, recrystallized from water and dried at 80–90°, gave the following result on analysis:

0.3552 gram substance gave 0.2297 gram silver.

	Theory for CH_3CO_2Ag	Found.
Ag	64.67	64.67

Sodic nitroethane has thus been split pretty smoothly, on treatment with an acid, according to the following equation:



$$2\,CH_3CH = \underset{\underset{O}{\|}}{N}{-}ONa + H_2SO_4 = 2\,CH_3CHO + N_2O + H_2O + Na_2SO_4.$$

The amount of acetaldehyde obtained (69.7% of the theory) is undoubtedly somewhat less than the actual amount formed in the reaction, since a slight loss of aldehyde can hardly be avoided in the above operations. It was shown qualitatively that nitrous acid, acetic acid, and hydroxylamine are side products in the above reaction. Entirely analogous results are obtained if hydrochloric acid, instead of sulphuric acid, is used in the reaction.

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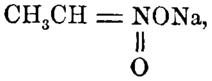
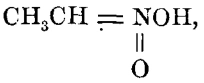
* A preliminary experiment with pure acetaldehyde showed that this method is well adapted for the quantitative determination of aldehyde. 1 gram acetaldehyde (bpt. 23°), 20 c.cm. water, and 8.3 grams silver oxide, heated in a sealed tube at 100° for one hour, gave 3.1 grams silver acetate corresponding to 81.7 per cent of the theory. Traces of unchanged aldehyde were noticed on opening the sealed tube.

The following explanation of this noteworthy decomposition of sodic nitroethane is extremely probable, especially because of facts to be presented later in this paper. On the addition of sodic nitroethane,



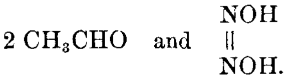
$$\mathrm{CH_3CH = \underset{\overset{\|}{O}}{N}ONa},$$

to a dilute acid, there is first formed the product



$$\mathrm{CH_3CH = \underset{\overset{\|}{O}}{N}OH},$$

which must be a strong oxidizing agent, and which therefore splits, just as in analogous cases to be presented below, by intramolecular oxidation into



$$2\ \mathrm{CH_3CHO} \quad \text{and} \quad \begin{matrix}\mathrm{NOH} \\ \| \\ \mathrm{NOH.}\end{matrix}$$

V. Meyer states * that on addition of an acid to aqueous sodic nitroethane, or to a caustic alkaline solution of nitroethane, free nitroethane is formed. Later he mentions † that acids never regenerate the entire amount of nitroethane from a solution of this substance in caustic potash, and that ethylnitrolic acid is always formed in small quantity. He seems never to have noticed a decomposition into acetaldehyde and nitrous oxide, which however always takes place, as is evident from the following experiments.

20 grams nitroethane are dissolved in a solution of 20 grams caustic potash ($1\frac{1}{3}$ molecules) in 300 c.cm. of water: the smell of nitroethane is still distinctly noticeable. To this solution is added very slowly dilute sulphuric acid, taking care to cool well with water. As soon as the solution becomes acid, it is colored greenish, and a gas evolution (N_2O) and strong smell of acetaldehyde are noticed. Since no nitroethane separates out, the solution is extracted three times with ether. The ethereal solution, after drying with calcic chloride, is then carefully fractionated; the lower boiling portions smell strongly of acetaldehyde. 7.2 grams oil were obtained, boiling between 112° and 118°, which, redistilled, gave 5.2 grams, boiling between 112° and 116°. The oil, although it smells of aldehyde, undoubtedly consists chiefly

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* Ann. Chem. (Liebig), CLXXI. 27-30. Cf. also Ber. d. chem. Ges., V. 514-516.

† Ann. Chem. (Liebig), CLXXV. 88-90.

of nitroethane, since on treatment with sodic nitrite 5 grams of ethylnitrolic acid were obtained from it.

An entirely analogous result is obtained on adding very slowly dilute sulphuric or hydrochloric acid to an aqueous solution of sodic nitroethane (made by means of sodium ethylate).

It is also possible to obtain traces of nitroethane on adding very slowly an aqueous solution of the sodium salt to dilute sulphuric acid. cooled with pieces of ice. The chief reaction in this case is, however, decomposition into acetaldehyde and nitrous oxide.

Decomposition of Nitroethane-mercuric-chloride by means of Acids.

Nitroethane-mercuric-chloride was obtained by addition of corrosive sublimate (one molecule) to an aqueous solution of sodic nitroethane. Since V. Meyer determined only the percentage of chlorine and mercury in the salt,* the substance, after drying for 24 hours in a vacuum, was analyzed for carbon and hydrogen.

0.6849 gram substance gave 0 1949 gram CO_2 and 0.0813 gram H_2O.

	Theory for $C_2H_4NO_2HgCl$.	Found.
C	7.75	7.76
H	1.30	1.34

The former statements concerning the properties of this salt could be confirmed except in one particular. V. Meyer mentions * that acids regenerate nitroethane. I found it impossible, under any condition, to obtain from this salt even a trace of nitroethane.

Dilute nitric acid and sulphuric acid act upon the salt very slowly in the cold, forming acetaldehyde and nitrous oxide: dilute hydrochloric acid reacts with great violence upon it, decomposing it into nitrous oxide and acetaldehyde. A large amount of the mercury salt, suspended in water, was treated in the cold with hydrogen sulphide, and thereupon the solution was partially distilled off. The distillate contained an oil which is neutral and smells strongly of thioaldehyde, but in which not a trace of nitroethane could be detected by means of the very delicate ethylnitrolic acid reaction.

As mentioned above, nitroethane-mercuric-chloride is decomposed by addition of dilute hydrochloric acid into nitrous oxide and acetaldehyde; the reaction is accompanied by a decided evolution of heat, and a greenish-colored solution is obtained. The quantitative determinations were carried out in the same apparatus as that used above in the case of the sodium salt. The mercury salt is placed in the distilling flask, and 10–15 c.cm. water added; after removing the air, dilute hydrochloric acid is added by means of the separatory funnel, and the solution is then heated to boiling. In the case of the aldehyde determination, the distillate is treated with powdered calcic carbonate, in order to remove the hydrochloric acid carried over, and then redistilled.

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* Ann. Chem. (Liebig), CLXXI. 31.

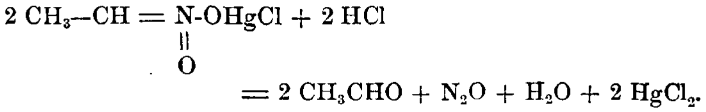
1 gram salt gave 39 c.cm. N_2O at 23° and 748 mm., corresponding to 98 per cent of the theory.
1 gram salt gave 38 c.cm. N_2O at 22° and 748 mm., corresponding to 95.6 per cent of the theory.
4.5 grams salt gave 1.77 grams silver acetate, i. e. 72.9 per cent of the theoretical amount.

The analysis of the silver acetate, recrystallized from water, gave the following result.

0.3831 gram substance gave 0.2468 gram silver.

	Theory for CH_3CO_2Ag.	Found.
Ag	64.67	64.42

Nitroethane-mercuric-chloride has thus been split by the acid, chiefly according to the following equation:



$$2\,CH_3\text{—}CH = \underset{\underset{\displaystyle O}{\|}}{N}\text{-}OHgCl + 2\,HCl$$
$$= 2\,CH_3CHO + N_2O + H_2O + 2\,HgCl_2.$$

Nitrous acid and hydroxylaminehydrochloride (0.4 gram crude salt from 10 grams) are side products formed in this decomposition.

Decomposition of Sodic Nitromethane by means of Acids.

Sodic nitromethane can be obtained from nitromethane by treating it in absolute ethereal solution with sodium wire, or by means of alcoholic sodic hydrate according to the method of V. Meyer. It is, however, best formed by addition of an alcoholic solution of sodium ethylate to an alcoholic solution of nitromethane. 30 grams nitromethane yield thus regularly from 45 to 50 grams of the sodium salt, which at first contains, as V. Meyer has shown, one molecule of alcohol,

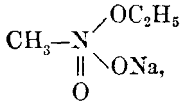
$$CH_2NO_2Na + C_2H_6O\,;$$

the salt slowly loses its alcohol on standing over sulphuric acid in a vacuum, but never completely. An analysis of a salt, which had been kept 14 hours in a desiccator, gave the following figures

0.2500 gram gave 0.1791 gram Na_2SO_4.

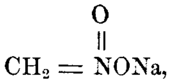
	Theory for CH_2NO_2Na.	Theory for $CH_2NO_2Na + C_2H_6O$.	Found.
Na	27.71	17.83	23.21

The constitution of this alkoholate is very probably



formed by the addition of the sodium ethylate to the nitro group.

Sodic nitromethane, free from alcohol,



$$CH_2 = \overset{\overset{\displaystyle O}{\|}}{N}ONa,$$

which is best obtained by treating nitromethane in ethereal solution with sodium, is a very unstable and remarkable body, which seems to exist only under great tension. On adding a small amount of water to it, spontaneous decomposition, with tremendous evolution of heat and ofttimes explosion, takes place.* On allowing an aqueous solution of the salt to evaporate spontaneously, it is decomposed chiefly into sodic carbonate and sodic nitrite (besides other products). The alcoholate of sodic nitromethane is much more stable than the pure sodium salt, but behaves otherwise in an entirely analogous manner. On adding an aqueous solution of either of these salts to dilute sulphuric acid or hydrochloric acid, decomposition into nitrous oxide, formaldehyde, nitrous acid, carbonic acid, and hydroxylamine takes place, and *not a trace of nitromethane is regenerated.*

The amount of nitrous oxide formed is small, as is evident from the following determinations.

2 grams sodium salt, made by means of sodium ethylate and kept a long time in a vacuum, gave 20 c.cm. N_2O at 20° and 752 mm., corresponding to 7.44 per cent of the theory for CH_2NO_2Na.

3 grams sodium salt, made by means of sodium ethylate and used directly, gave 26 c.cm. N_2O at 22°, and 748 mm., corresponding to 7.48 per cent of the theory for $CH_2NO_2Na + \frac{1}{2}\, C_2H_6O$.

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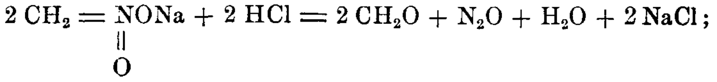
* Ann. Chem. (Liebig), CLXXI. 34.

In the decomposition of sodic nitromethane by acids, a splitting takes place, but in subordinate amount, according to the equation



$$2\,CH_2=\underset{\underset{O}{\|}}{N}ONa+2\,HCl=2\,CH_2O+N_2O+H_2O+2\,NaCl;$$

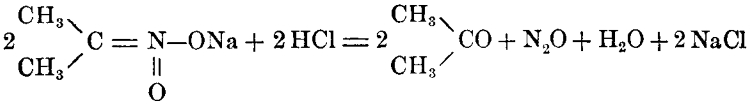
which is entirely analogous to the decomposition of nitroethane salts. The reason for this difference is also perfectly clear and will be explained farther on.

It is possible, but only under very special conditions and in subordinate amounts, to regenerate nitromethane from its sodium salt;* in all cases a very decided decomposition takes place, as will become evident from the following experiments. 10 grams sodic nitromethane, made by means of sodium ethylate and kept 10 hours in a vacuum over sulphuric acid, are dissolved in water containing pieces of ice, and then dilute sulphuric acid is added very slowly. As soon as the solution becomes acid, a smell of formaldehyde is noticed, as well as the presence of nitrous acid and of nitrous oxide and carbon dioxide. 20 c.cm. of the solution † is then distilled off (until no smell of nitromethane can be noticed in the flask) and the distillate extracted with ether. The ethereal solution, carefully fractionated, gave 1.9 grams nitromethane, boiling between 99° and 101°. An entirely analogous result is obtained from a solution of nitromethane in caustic soda or potash.

Decomposition of Secondary Sodic Nitropropane by Acids.

Secondary nitropropane was made according to the directions of V. Meyer.‡ The yield is very poor. The sodium salt was made by means of alcoholic sodium ethylate, and dried over sulphuric acid in a vacuum.

On treatment of an aqueous solution of this salt with dilute acids, a fairly smooth decomposition into acetone and nitrous oxide, according to the equation



$$2\begin{matrix}CH_3\diagdown\\CH_3\diagup\end{matrix}C=\underset{\underset{O}{\|}}{N}-ONa+2\,HCl=2\begin{matrix}CH_3\diagdown\\CH_3\diagup\end{matrix}CO+N_2O+H_2O+2\,NaCl$$

takes place, — a reaction which is perfectly analogous to the decomposition of salts of primary nitroparaffines.

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* No statements concerning this point could be found anywhere.

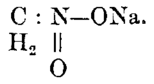
† Preibisch, Journ. f. prakt. Chemie, [2.], VIII. 311.

‡ Ann. Chem. (Liebig), CLXXI. 40

0.7 gram sodium salt, dissolved in water and added in the above apparatus to 15 c.cm. dilute sulphuric acid, gave (the solution becomes colored greenish) 51 c.cm. N_2O at 21° and 754 mm., corresponding to 66.52 per cent of the theory.

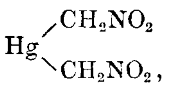
The formation of acetone in this reaction was proved as follows. 1.9 grams secondary sodic nitropropane are dissolved in water and added to 15 c.cm. dilute sulphuric acid. The bluish green solution is heated to boiling and partially distilled off. The distillate is filtered from a small amount of solid and treated with powdered calcic carbonate and then redistilled. The solution thus obtained, which smells distinctly of acetone, is treated with a solution of 0.6 gram hydroxylamine hydrochloride and 0.34 gram caustic soda in 2.5 c.cm. water. After standing for an hour, the solution is extracted three times with ether, and after getting rid of the dried ether 0.35 gram residue is obtained. This was recrystallized from ligroine (bpt. 40°–60°) and found to melt at 62°–63°, and to consist of pure acetoxime, identical in every respect with a product made for comparison.

II. Synthesis of Mercury Fulminate, $C:NOhg$, from Sodic Nitromethane,



$$\begin{array}{l} \quad\ C:N{-}ONa. \\ H_2\ \ \ \| \\ \qquad\ O \end{array}$$

With the exception of nitroethane-mercuric-chloride, no heavy metal salt of a simple nitroparaffine has been obtained and analyzed. Victor Meyer and Rilliet obtained from sodic nitromethane and mercuric chloride a yellow very explosive mercury salt, which they regarded as mercury nitromethane,



but which, on account of its very dangerous properties,* was not further investigated or analyzed.

Since such heavy metal salts might perhaps be especially well adapted for a determination of the constitution of the nitroparaffine salts, a study of this salt was therefore again taken up, and it soon became evident that it is not a salt of nitromethane at all because it contains no hydrogen.

On adding quickly an aqueous solution of sodic nitromethane to a solution of corrosive sublimate, or *vice versa*, a white precipitate is first formed, which very soon becomes colored yellow, and which in all probability is the mercury salt of nitromethane,

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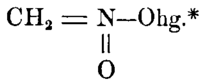
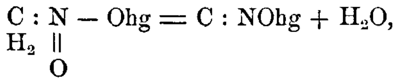
* Ber. d. chem. Ges., V 1030. Cf. Ann. Chem. (Liebig), CLXXI. 35.



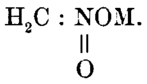
$$CH_2 = \underset{\overset{\|}{O}}{N}\text{--}Ohg.$$[*]

This white salt exists, however, only a few moments, since it is a very powerful oxidizing agent capable of intra-molecular oxidation. It therefore loses water almost instantly,



$$\underset{H_2}{C} : \underset{\overset{\|}{O}}{N} - Ohg = C : NOhg + H_2O,$$

forming mercuric fulminate; and since the constitution of fulminate of mercury is definitely proved in the following paper to be $C : NOhg$, it follows at the same time that the nitromethane salts must have the constitution represented by the general formula



$$H_2C : \underset{\overset{\|}{O}}{N}OM.$$

An aqueous solution of sodic nitromethane (10 grams) is added rapidly to a cold mercuric chloride solution (containing 16 grams $HgCl_2$). After standing 15 minutes, the solution (300–500 c.cm.) is heated to boiling and quickly filtered from the yellow precipitate, which is then boiled out once with hot water. On cooling, a grayish white heavy crystalline precipitate separates out from the filtrate. In order to get rid of traces of adhering mercury, it is dissolved in dilute cyanide of potash and reprecipitated with dilute nitric acid.[†] In this way perfectly pure fulminate of mercury is obtained, which is absolutely identical in every respect with the product made in the ordinary way. The yield is 1 gram to 1.6 grams pure salt from 10 grams sodic nitromethane.

0.2221 gram substance, dried over H_2SO_4 in a vacuum, and dissolved in dilute hydrochloric acid, with addition of $KClO_3$, and precipitated with H_2S, gave 0.1815 gram HgS.

0.4005 gram substance, mixed with cupric oxide, gave 0.1248 gram CO_2 and 0.0074 gram H_2O.

0.1968 gram substance gave 17.5 c.cm. N_2 at 16° and 747 mm.

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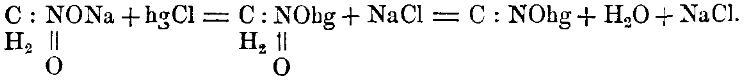
[*] hg represents a half-atom of bivalent mercury.

[†] Steiner, Ber. d. chem. Ges., IX. 787.

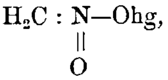
	Theory for $HgO_2N_2C_2$.	Found.
Hg	70.42	70.45
C	8.45	8.49
H	—	0.205
N	9.86	10.18

The following very simple reaction therefore takes place in the formation of mercuric fulminate from sodic nitromethane:



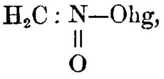
$$\underset{H_2}{C} : \underset{\underset{O}{\|}}{N}ONa + hgCl = \underset{H_2}{C} : \underset{\underset{O}{\|}}{N}Ohg + NaCl = C : NOhg + H_2O + NaCl.$$

It follows clearly, however, that the mercury salt of nitromethane,



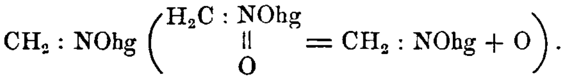
$$H_2C : \underset{\underset{O}{\|}}{N}{-}Ohg,$$

formed as the intermediate product, must be a strong oxidizing agent, which at first, for want of anything else present, acts on itself, forming by intra-molecular oxidation fulminate of mercury, C : NOhg. Since, however, the fulminate of mercury thus formed, in consequence of its containing unsaturated or bivalent carbon, possesses an enormous reactivity (see following paper) and can therefore most readily take up oxygen, (this explains the reducing action of carbon monoxide, C : O, of cyanide of potash, KN : C, as well as of the fulminates, C : NOM,) it follows very clearly that the strong oxidizing agent present, mercury nitromethane,



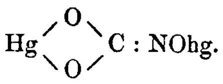
$$H_2C : \underset{\underset{O}{\|}}{N}{-}Ohg,$$

can act also on the mercury fulminate formed (in the nascent state), converting it into mercuric carbondioxidoxime, O : C : NOhg, whereby the mercuric nitromethane itself is reduced to mercuric formoxime,



$$CH_2 : NOhg \left(H_2C : \underset{\underset{O}{\|}}{N}Ohg = CH_2 : NOhg + O \right).$$

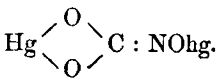
This explanation suffices completely in clearing up the nature of all the products which are formed by the interaction of sodic nitromethane and mercuric chloride. The yellow salt obtained by V. Meyer and Rilliet* is, in all probability, basic mercuric carbondioxidoxime,



$$\mathrm{Hg}{<}{\mathrm{O} \atop \mathrm{O}}{>}\mathrm{C} : \mathrm{NOhg}.$$

A yellow compound insoluble in water is, in all cases, the chief product of the action between aqueous solutions of sodic nitromethane and mercuric chloride; in fact only by the above mentioned method is it possible to obtain fulminate of mercury in appreciable amounts. If the corrosive sublimate solution is heated, before adding the sodic nitromethane solution, or if the former solution is added to the latter solution, not a trace of mercuric fulminate can be isolated, and much yellow insoluble mercury salt is formed. The composition of this yellow salt varies also according to whether the mercuric chloride solution is added to a solution of the sodium salt, or *vice versa.* In the latter case, the salt obtained contains much more carbon and nitrogen.

Basic Mercuric Carbondioxidoxime,



$$\mathrm{Hg}{<}{\mathrm{O} \atop \mathrm{O}}{>}\mathrm{C} : \mathrm{NOhg}.$$

On the addition of a solution of mercuric chloride (containing 16 grams $HgCl_2$) to a cold aqueous solution of sodic nitromethane (10 grams), a white precipitate is formed which, after an hour's standing, has become perfectly yellow. The solution is decanted, and the residue is repeatedly treated with boiling water, and then dried on clay plates, and finally at 100°. The latter operation must be carried on with all possible precautions, since it happened several times that the salt exploded, demolishing the air bath and the windows of the hood. The yield from 10 grams sodium salt was regularly from 8 to 10 grams. The salt is, at ordinary temperatures, not quite so dangerous as mercuric fulminate, but it often explodes by friction. It is absolutely free from chlorine and contains no hydrogen: digestion with dilute sulphuric or with dilute nitric acid, in which it is insoluble, does not change the composition of the salt.

0.4698 gram, mixed with cupric oxide, gave 0.0612 gram CO_2 and 0.0129 gram H_2O.

0.1818 gram, mixed with cupric oxide, gave 6.5 c.cm. N_2 at 19° and 747 mm.

0.2195 gram, dissolved in dilute hydrochloric acid, with addition of little $KClO_3$ and precipitated with H_2S, gave 0.2045 gram HgS.

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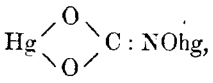
[*] Ber. d. chem. Ges., V. 1030. Cf. Ann. Chem. (Liebig), CLXXI. 35.

	Theory for $\mathrm{Hg}\left\langle\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}\right\rangle\mathrm{C:NOhg}$	Found.
C	3.21	3.34
H	—	0.305
N	3.74	4.04
Hg	80.20	80.31

The salt is instantly decomposed by dilute hydrochloric acid. forming calomel, carbonic acid, and a substance having a smell like prussic acid, but not a trace of nitrous oxide is formed. Concentrated hydrochloric acid decomposes the salt into carbonic acid and hydroxylaminehydrochloride (proved by conversion into acetoxime). The salt is very soluble in dilute cyanide of potash, and on addition of dilute nitric acid no precipitate is formed. It was at first long suspected that the salt was basic fulminate of mercury, but it is not possible in any way to convert this salt into normal fulminic acid salts. Thus a large quantity of it was added to hydrochloric acid (one part conc. acid 1.18 to one part water), and the solution thereupon extracted with ether, but not a trace of formylchloridoxime (see following paper) was obtained. On treating the salt suspended in water with sodium amalgam, mercury is formed, and a solution obtained free from mercury, in which, however, not a trace of sodium fulminate could be detected.

That the salt possesses the constitution,



$$\mathrm{Hg}\left\langle\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}\right\rangle\mathrm{C:NOhg},$$

is very probable, but not yet proved with absolute certainty. It will therefore be further investigated, especially since its behavior towards alkyliodides and its conversion into carbondioxidoxime, $O : C : NOH$, may be of interest.

As mentioned above, there is formed, on addition of aqueous sodic nitromethane to a mercuric chloride solution, besides fulminate of mercury, a yellow insoluble salt, which is richer in carbon and in nitrogen than the yellow salt just described.

This yellow salt, precipitated from hot mercuric chloride solution, was repeatedly digested with boiling water and then dried, first on a clay plate, and then *carefully* at 100°.

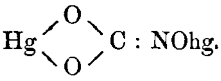
The substance is likewise free from chlorine and hydrogen and explodes very readily by friction.

0.6731 gram, mixed with cupric oxide, gave 0.1487 gram CO_2 and 0.0236 gram H_2O.

0.2776 gram gave 16 c.cm. N_2 at 15° and 749 mm.

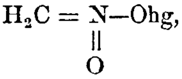
	Theory for $Hg\langle{}^{O}_{O}\rangle C : NOhg$	Theory for $O : C : NOhg$	Found.
C	3.21	7.59	6.03
H	—	—	0.39
N	3.74	8.86	6.65

This salt behaves in every respect — towards dilute nitric, hydrochloric, and sulphuric acid, towards concentrated hydrochloric acid, sodium amalgam, and cyanide of potash — in exactly the same manner as the mercury salt just described. It probably consists therefore of a mixture of much mercuric carbondioxidoxime, O : C : NOhg and of the basic salt,



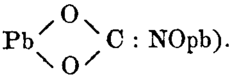
It is natural that in this case much less basic salt should be formed than in the former case, where the corrosive sublimate solution was added to the sodic nitromethane solution.

The above experiments have made it clear that the heavy metal salts of nitromethane, e. g. a mercury salt,

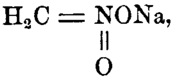


$$H_2C = \underset{\overset{\|}{O}}{N}\text{—}Ohg,$$

are not capable of existence, but are immediately decomposed by intramolecular oxidation. An investigation of the precipitates formed by adding copper sulphate or lead acetate to an aqueous solution of sodic nitromethane showed that these consist in great part either of copper carbonate or of lead carbonate (the lead salt obtained is yellow and explodes, and probably contains some



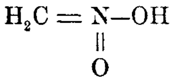
For these reasons it is obvious that sodic nitromethane itself,



$$H_2C = \underset{\overset{\|}{O}}{N}ONa,$$

which, as is known, exists only under great tension, must be a strong oxidizing agent which can easily, by intra-molecular oxidation, go over into O : C : NONa and CH_2 : NONa,* which products in turn are readily split into carbonic acid, hydroxylamine nitrous acid, and other compounds. This explains therefore most clearly the intensely violent decomposition of this salt on addition of a small quantity of water, as well as its decomposition, in dilute aqueous solutions, into sodic carbonate, sodic nitrite, and other products.

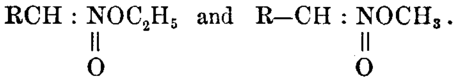
On adding sodic nitromethane to dilute acids, the product



$$H_2C = \underset{\underset{O}{\|}}{N}-OH$$

is in all probability first formed, which must readily go over, by intra-molecular oxidation, into O : C : NOH and CH_2 : NOH, or into their decomposition products. A slight decomposition, however, into 2 CH_2O and N_2O also takes place, — which in the case of the other primary and the secondary nitroparaffine salts is the chief reaction (see above).

The formation of the above mentioned remarkable decomposition products of nitroparaffine salts, which, as is clearly seen, is due solely to intra-molecular oxidation, find further on their complete analogy in the decomposition products of esters of the formula,



$$RCH : \underset{\underset{O}{\|}}{N}OC_2H_5 \quad \text{and} \quad R-CH : \underset{\underset{O}{\|}}{N}OCH_3 .$$

These substances also decompose (some spontaneously) by intra-molecular oxidation into RCH : NOH and CH_3CH : O or CH_2O.

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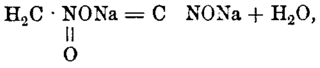
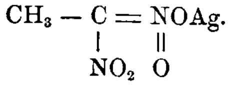
* The fulminate of soda, C : NONa, which is first formed as an intermediate product,



$$H_2C \cdot \underset{\underset{O}{\|}}{N}ONa = C \quad NONa + H_2O,$$

must naturally be converted immediately by the excess of sodic nitromethane present into O : C : NONa, and thus it in turn be reduced to CH_2 : NONa. It was not possible at any rate, under any condition, to convert sodic nitromethane by loss of water into sodium fulminate, — a fact which in view of the enormous tendency of this salt to take up oxygen is almost self-evident.

III. THE ACTION OF ALKYLIODIDES ON SILVER DINITROETHANE,



$$CH_3 - \underset{NO_2}{\underset{|}{C}} = \underset{O}{\underset{\|}{N}}OAg.$$

Preparation of Dinitroethane. — After many experiments, the following method of preparing dinitroethane was found to give the best results.* 50 grams bromnitroethane (bpt. 140–145°, prepared according to the directions of Tscherniak †), 50 c.cm. alcohol, and a solution of 56 grams potassic nitrite in 56 grams water, were kept shaken up very thoroughly in a shaking apparatus for 24 hours. The potassium salt of dinitroethane separates out slowly in yellow crystals, which, when filtered off and well washed with alcohol, are sufficiently pure. The yield is from 13 to 14 grams. The salt is dissolved in warm water and treated directly with silver nitrate (one molecule), and the silver salt obtained in glistening heavy yellow leaflets, which are filtered off and dried in a vacuum.

Ter Meer ‡ has already studied the behavior of this salt towards methyliodide and obtained thereby an oil, which, on treatment with alcoholic potash, is partially converted back again into potassic dinitroethane. Very recently Duden has studied the behavior of silver dinitromethane towards alkyliodides, § and shown that, for example, it is converted by means of methyliodide into dinitroethane.

The reaction which takes place, however, on treating the silver salt of dinitromethane and of dinitroethane with alkyliodides, is far more complicated than either ter Meer or Duden have surmised; the very remarkable and peculiar reaction is cleared up fully by the following experiments.

50 grams silver dinitroethane are added slowly to 100 grams methyliodide, taking care to cool well with water. Reaction quickly takes place, with formation of silveriodide, and, towards the end, a strong smell of formaldehyde is noticed. After standing one hour, ether is added and the excess of methyliodide as well as the ether is removed from the filtrate by heating in a distilling flask at 50 mm. pressure to a temperature of 50°. The residual oil is taken up with ether, and treated with cold dilute sodic hydrate and the deep red colored alkaline solu-

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* Ter Meer, Ann. Chem. (Liebig), CLXXXI. 6; Chancel, Jahresber., 1883, p. 1039.

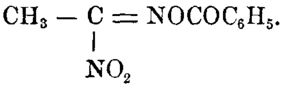
† Ann. Chem. (Liebig), CLXXX. 126. ‡ Ibid., CLXXXI. 16.

§ Ber. d. chem. Ges., XXVI. 3003.

tion immediately acidified with dilute sulphuric acid and extracted with ether. After drying the ethereal solutions with calcic chloride, and getting rid of the ether at reduced pressure, 10.1 grams of neutral products and 9 grams of acid products are obtained.

On allowing the oily acid portion to stand in the air, crystals of ethylnitrolic acid (1 gram) separated out, and the oil gave, on treatment with alcoholic potash, 5.3 grams of potassic dinitroethane, which was filtered off. The deep red colored filtrate gave, on acidifying and extracting with ether, 0.4 gram more of ethylnitrolic acid. The acid products formed in the above reaction are therefore dinitroethane and ethylnitrolic acid. The latter substance melted at 88°, and was identical in every respect with a preparation made from nitroethane.* This substance gives on treating in alkaline solution with benzoylchloride † a characteristic insoluble benzoate.

Ethylnitrolic Acid Benzoate,



$$CH_3 - \underset{\displaystyle NO_2}{\underset{|}{C}} = NOCOC_6H_5.$$

12.1 grams ethylnitrolic acid, dissolved in 46 c.cm. sodic hydrate (1 : 10), and shaken with 16.4 grams benzoylchloride gave 21.6 grams crude benzoate (calculated 24.2 grams). Crystallized twice from benzene, and twice from alcohol, it is obtained in colorless flat needles, melting at 135°; it is easily soluble in hot benzene and alcohol, and very slightly in ether. It is insoluble in water, and is decomposed slowly on standing with sodic hydrate into benzoic acid and ethylnitrolic acid.

0.1585 gram, dried at 70°, gave 0.3001 gram CO_2 and 0.0604 gram H_2O.
0.1995 gram, dried at 70°, gave 24 c.cm. N_2 at 16° and 750 mm.

	Theory for $C_9H_8N_2O_4$	Found.
C	51.92	51.64
H	3.85	4.23
N	13.46	13.84

The above mentioned portion (10.1 grams), insoluble in alkalies, is also a mixture of two substances. It was first distilled with steam, whereby all but a trace of yellow sticky material is easily carried over; the first portions of the distillate contain oil drops, which do not solidify, and the latter portions contain a substance which solidifies in the condenser, so that it is possible already at this point to accomplish a partial separation of the two products. The distillate was, however, extracted with ether; and the ethereal solution was washed with dilute sodic hydrate, and, after drying with calcic chloride, the ether was distilled off. 9.2 grams of oil were obtained, which was fractioned under reduced pressure. The first portions boiled between 78° and 85° at 30 mm. pressure and were oily; as soon as the distillate begins to solidify, the operation was discontinued, and the residue in the distilling flask (4.25 grams) poured out. On cooling, this solidified completely. It was transferred to a clay plate, and washed with a small amount of ligroine, and thus 2.8 grams perfectly pure β dinitropropane, melting at 55°, were obtained, identical in every particular with the product obtained by V. Meyer and Locher.*

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* Ann. Chem. (Liebig), CLXXV 94; CLXXXI. 2.

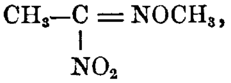
† Baumann and Udranzsky, Ber. d. chem. Ges., XXI. 2744.

0.2185 gram, dried over H_2SO_4 in a vacuum, gave 0.2141 gram CO_2 and 0.0941 gram H_2O.

0.2272 gram gave 43.5 c.cm. N_2 at 24° and 753 mm.

	Theory for $(CH_3)_2 : C(NO_2)_2$.	Found.
C	26.86	26.72
H	4.48	4.79
N	20.90	21.27

The lower boiling oil, which is not volatile without decomposition at ordinary pressure, and which is more volatile with steam than β dinitropropane, was not analyzed, as it still contained traces of β dinitropropane. That it consists, however, of ethylnitrolic acid methylester,



$$CH_3{-}\underset{\displaystyle NO_2}{\underset{|}{C}}{=}NOCH_3,$$

is very probable, and a number of experiments were therefore carried out with the object of isolating this substance directly from the silver and lead salts of ethylnitrolic acid by means of methyliodide, which, however, failed on account of the great instability of the ethylnitrolic acid salts in the presence of water.†

On adding 11 grams of silver dinitroethane to 50.5 grams ethyliodide, reaction sets in immediately, and at the end a very strong smell of acetaldehyde is noticed. Both neutral and acid products are formed:

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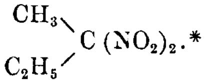
* Ann. Chem. (Liebig), CLXXX. 147.

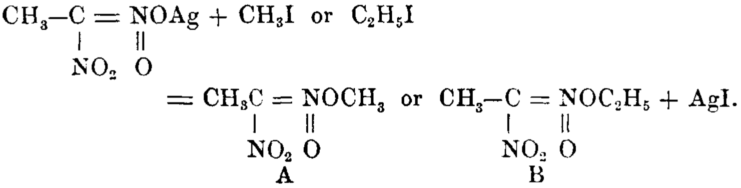
† V. Meyer, Ann. Chem. (Liebig), CLXXV. 103.

the presence of ethylnitrolic acid and of dinitroethane in the acid portion was proved as in the above case. The neutral portion was an oily mixture, boiling between 105° and 130° at 30 mm. pressure. The amount of material at hand was, however, insufficient to admit of its further study, although a portion boiled at ordinary pressure at about 200°, and consists therefore probably of β dinitrobutane,



The results obtained above prove that the reaction which takes place on treating silver dinitroethane with alkyliodides is the following.

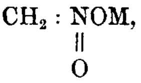
I. Direct replacement of the metal (chief reaction):



$$CH_3{-}\underset{\substack{|\\ NO_2}}{C}=\underset{\substack{\|\\ O}}{N}OAg + CH_3I \text{ or } C_2H_5I$$

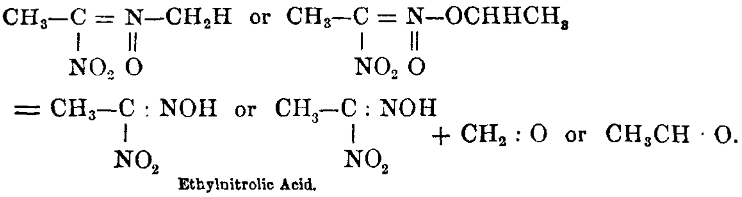
$$= \underset{A}{CH_3\underset{\substack{|\\ NO_2}}{C}=\underset{\substack{\|\\ O}}{N}OCH_3} \text{ or } \underset{B}{CH_3{-}\underset{\substack{|\\ NO_2}}{C}=\underset{\substack{\|\\ O}}{N}OC_2H_5} + AgI.$$

The esters A and B, which are first formed, are however very unstable compounds, and just as the nitromethane salts,



$$CH_2 : \underset{\substack{\|\\ O}}{N}OM,$$

are strong oxidizing agents. An intramolecular oxidation therefore takes place, and ethylnitrolic acid and either formaldehyde or acetaldehyde is formed, according to the equation:



$$CH_3{-}\underset{\substack{|\\ NO_2}}{C}=\underset{\substack{\|\\ O}}{N}{-}CH_2H \text{ or } CH_3{-}\underset{\substack{|\\ NO_2}}{C}=\underset{\substack{\|\\ O}}{N}{-}OCHHCH_3$$

$$= \underset{\text{Ethylnitrolic Acid.}}{CH_3{-}\underset{\substack{|\\ NO_2}}{C} : NOH} \text{ or } CH_3{-}\underset{\substack{|\\ NO_2}}{C} : NOH + CH_2 : O \text{ or } CH_3CH \cdot O.$$

The ethylnitrolic acid thus formed reacts upon silver dinitroethane, present in excess, setting free dinitroethane and forming the silver salt of ethylnitrolic acid,

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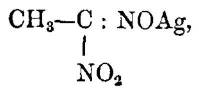
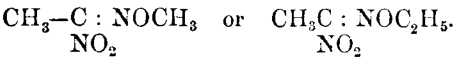
* V Meyer, Ber. d. chem. Ges., IX. 701.



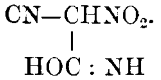
$$\begin{array}{l}CH_3\text{—}C : NOAg,\\ \qquad\;\; | \\ \qquad NO_2\end{array}$$

which then reacts with the iodide of methyl or ethyl, forming either the methyl ester or the ethyl ester of ethylnitrolic acid,



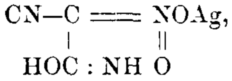
$$\begin{array}{lcl}CH_3\text{—}C : NOCH_3 & \text{or} & CH_3C : NOC_2H_5.\\ \quad\;\; NO_2 & & \quad\;\; NO_2\end{array}$$

That this explanation of the reaction is the correct one, is proved with certainty by the following fact: fulminuric acid is, as will be shown in the paper presented directly after this one, identical with nitrocyanacetamide,



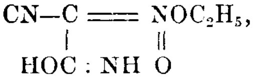
$$\begin{array}{c}CN\text{—}CHNO_2.\\ |\\ HOC : NH\end{array}$$

On treating the silver salt of this substance,



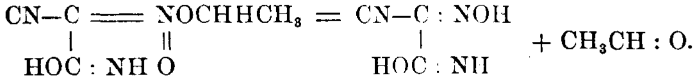
$$\begin{array}{lcl}CN\text{—}C & = & NOAg,\\ \quad\;\; | & & \;\; \Vert\\ HOC : NH & & \;\; O\end{array}$$

with ethyliodide, there is formed, by direct replacement of the silver, the ester,



$$\begin{array}{lcl}CN\text{—}C & = & NOC_2H_5,\\ \quad\;\; | & & \;\; \Vert\\ HOC : NH & & \;\; O\end{array}$$

which, in this case, can be isolated. This compound is, however, very unstable, and shows, just as the above assumed intermediate products (A and B) and as the nitromethane salts, great tendency to intramolecular oxidation. On boiling with water it is split quantitatively into acetaldehyde and cyanisonitrosoacetamide (see following paper).



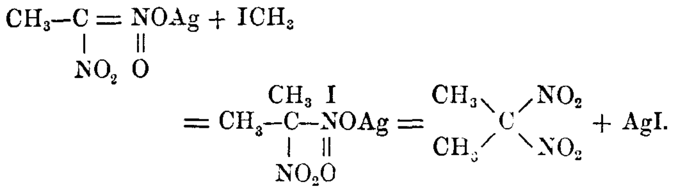
$$\begin{array}{lcl}CN\text{—}C & = & NOCHHCH_3\\ \quad\;\; | & & \;\; \Vert\\ HOC : NH & & \;\; O\end{array} = \begin{array}{c}CN\text{—}C : NOH\\ |\\ HOC : NH\end{array} + CH_3CH : O.$$

Cyanisonitrosoacetamide.

This decomposition is perfectly analogous to those above.

The formation of β dinitropropane from silver dinitroethane and methyliodide is in all probability to be explained by an addition of methyliodide to the silver salt of dinitroethane:

II.



There are now so many cases known, where, by the interaction of silver salts with alkyliodides or acid chlorides, no direct or only partially a direct replacement of the silver takes place,* that this explanation is not at all improbable, — especially also when one considers the remarkable behavior of silver fulminate towards hydrogen sulphide and towards hydrochloric acid (see following paper).

The formation of formic aldehyde, ethylnitrolic acid, dinitroethane, β dinitropropane and of a fifth compound, probably ethylnitrolic acid methylester, on treating silver dinitroethane with iodide of methyl, is therefore perfectly cleared up by the above considerations.

IV. THE ACTION OF ACID CHLORIDES ON NITROPARAFFINE SALTS.

The former experiments on the action of acetylchloride and of benzoylchloride on sodic nitromethane and on sodic nitroethane † have led to no positive results. Kissel has shown ‡ that in these reactions some dibenzhydroxamic acid and diacethydroxamic acid is formed, but these can only have been formed, however, by a complete destruction of the nitroparaffine molecule.

I have also carried out many fruitless experiments on these salts with acetylchloride and benzoylchloride, and also with chlorocarbonic ether; both neutral and acid products are formed, which cannot be solidified, and which do not distil under reduced pressure without decomposition. Entirely analogous results were obtained by the action of acetylchloride and benzoylchloride on nitroethane-mercuric-chloride,

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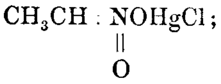
* Ann. Chem. (Liebig), CCLXX. 329, 331; CCLXXVI. 232; CCLXXVII. 73. The experiment with silver acetylacetone has been carried out here by Dr. Curtiss with larger quantities of material, and both products have been analyzed.

† V. Meyer and Rilliet, Ber. d. chem. Ges., V. 1030; VI. 1168.

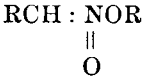
‡ Ber. d. chem. Ges., XV. Ref. 727 and 1574.



$$\mathrm{CH_3CH:\underset{\underset{O}{\|}}{N}OHgCl;}$$

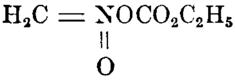
both these reagents, and especially the former, act with explosive violence on this salt, so that it is necessary to dilute with absolute ether.

The above results with silver dinitroethane, which have shown that neutral ethers of the constitution



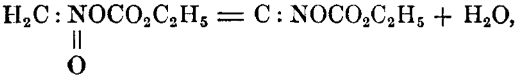
$$\mathrm{RCH:\underset{\underset{O}{\|}}{N}OR}$$

must be strong oxidizing agents, encourage one to undertake a renewed study of the action of acid chlorides on nitroparaffine salts, and experiments will therefore very shortly be taken up again. Of especial interest is the behavior of chlorocarbonic ether towards sodic nitromethane. It is to be expected that the ester



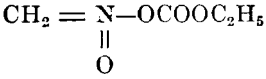
$$\mathrm{H_2C = \underset{\underset{O}{\|}}{N}OCO_2C_2H_5}$$

will at first be formed, and this compound must, by intramolecular oxidation, lose water, and be converted into carbyloximecarbonic ester,



$$\mathrm{H_2C:\underset{\underset{O}{\|}}{N}OCO_2C_2H_5 = C:NOCO_2C_2H_5 + H_2O,}$$

which then will be further oxidized by the ester



$$\mathrm{CH_2 = \underset{\underset{O}{\|}}{N}{-}OCOOC_2H_5}$$

to carbondioxydoximecarbonic ester, $\mathrm{O:C:NOCO_2C_2H_5}$, and at the same time thus formoximecarbonic ester, $\mathrm{CH_2:NOCO_2C_2H_5}$, will be formed.

Concluding Remarks.

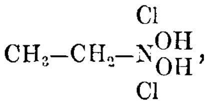
The above experiments suffice to prove, with absolute precision, that the metal in the nitroparaffine salts is bound to oxygen, and not, as has been previously supposed, to carbon; and in consequence, the hypothesis that there are organic substances of an acid nature, in whose salts the metal is bound to carbon, is no longer tenable. Its conception has been shown to be illogical,* and the work that I have carried out during the last six years has proved, by incontrovertible experimental evidence, the erroneousness of this hypothesis in all cases where it has been applied.

The only instances of organic compounds now known which contain a metal bound directly to carbon are the metallic carbides, the metallic alkyles, and the metallic derivatives of the true acetylene compounds. No one would however be willing to assert that these substances are salts of acids. Acetylene, for example, is not an acid, for it is not absorbed with salt formation by even concentrated caustic alkalies. The peculiar formation of the metallic acetylene derivatives, e. g. of acetylene silver or copper, depends, in all probability, upon an addition of metallic hydroxide to the triple bond present in acetylene, and the subsequent splitting off of water.

As regards the constitution of the free nitroparaffines, the presence of a true nitro group in these compounds can hardly be seriously questioned, especially in view of the experiments of Victor Meyer † and the late syntheses carried out by Bewad.‡

The formulæ suggested for nitroethane by Geuther,§ Kissel,‖ Alexejeff,¶ and Thomsen,** owe their existence chiefly to the very noteworthy decomposition of nitroethane into acetic acid and hydroxylamine, when treated with concentrated hydrochloric acid.††

This decomposition of nitroethane can now, because of the above experiments, be easily explained. An addition of hydrochloric acid to the nitro group, analogous to the addition of sodic hydrate or sodium ethylate, first takes place, forming



$$CH_3{-}CH_2{-}\overset{Cl}{\underset{Cl}{N}}{\begin{smallmatrix}OH\\OH\end{smallmatrix}},$$

which then loses hydrochloric acid

$$CH_3C \equiv N{\begin{smallmatrix}OH\\OH\end{smallmatrix}},$$

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* These Proceedings, XXVII. 157.

† Ann. Chem. (Liebig), CLXXI., etc.

‡ Journ f. prakt. Chemie, [2.]. XLVIII. 346.

§ Ann. Chem. (Liebig), CCXLIII. 105.

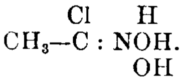
‖ Journ. russ. chem. Soc., XIV. 40.

¶ Ber. d. chem. Ges., XIX. Ref. 874.

** Journ. f. prakt. Chemie, [2.], XLVIII. 348.

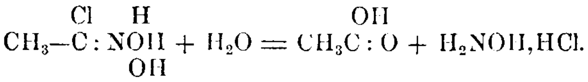
†† V. Meyer and Locher, Ann. Chem. (Liebig), CLXXX. 163.

and then again adds hydrochloric acid



$$CH_3-\overset{Cl}{C}:\overset{H}{\underset{OH}{N}}OH.$$

This product can then easily split into acetic acid and hydroxylamine,



$$CH_3-\overset{Cl}{C}:\overset{H}{\underset{OH}{N}}OH + H_2O = CH_3\overset{OH}{C}:O + H_2NOH,HCl.$$

In the above experiments I have been most ably and zealously assisted by Dr. M. Ikuta, to whom I wish here also to express my warmest thanks.

VI.

CONTRIBUTIONS FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.

ON BIVALENT CARBON.

SECOND PAPER.*

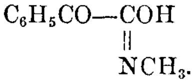
By J. U. Nef.

Presented May 9, 1894.

The bivalent carbon atom in methyl- and in ethyl-isocyanide shows itself much more reactive, as was to be expected, than in the case of the aromatic isocyanides. The reactions, however, are otherwise entirely analogous to those obtained in the case of the aromatic compounds, as is evident from the following experiments.

I. On Ethyl and Methyl Isocyanide.

Benzoylformic Methylamide,



$$C_6H_5CO—\underset{\displaystyle NCH_3.}{\underset{\|}{COH}}$$

The methylisocyanide used was made according to the method of Gautier,† by heating 100 grams silver cyanide and 100 grams methyl-iodide for two hours on a water bath (with reversed condenser and with a mercury valve). This substance unites with benzoylchloride slowly already at ordinary temperatures, as is recognized by the yellow coloration which sets in. 10.2 c.cm. methylisocyanide and 27 grams benzoylchloride (one molecule) are mixed and heated for half an hour at 100° in a sealed tube. No more isonitrile is left, and longer heating is harmful, since much formation of resin (polymerization) then takes place. The crude product is taken up with absolute ether, filtered off from brown resinous flakes, and the residual oil, after getting rid of the ether, treated with water, whereby on standing, or rubbing with a glass rod, it becomes solid. The substance is recrystallized from a mixture of ether and ligroine (bpt. 40° to 60°), using animal charcoal, and obtained in pale yellow heavy many-sided crystals, melting at 74°. It is little soluble in cold, but readily soluble in hot water, and comes out on cooling in prisms. In organic solvents, except ligroine, it is easily soluble.

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* First Paper, these Proceedings, XXVII. 102-162.

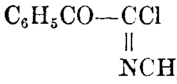
† Annales de Chim. et de Phys., [4.], XVII. 216.

0.1970 gram dried over H_2SO_4 in a vacuum gave 0.4775 gram CO_2 and 0.1044 gram H_2O.

0.2034 gram gave 15.5 c.cm. N_2 at 4° and 735 mm.

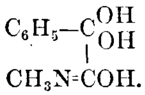
	Theory for $C_9H_9NO_2$.	Found
C	66.25	66.11
H	5.52	5.88
N	8.59	9.05

Benzoylformic-methylamide has thus been obtained from the addition product



$$C_6H_5CO{-}\underset{\displaystyle NCH_3}{\overset{}{C}}Cl \quad (C{=}NCH_3)$$

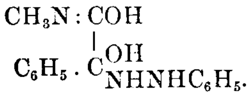
first formed. The substance is easily soluble in cold dilute sodic hydrate, but on addition of dilute sulphuric acid it is not precipitated again. Ether extracts an oily substance soluble in water, which slowly, on standing over sulphuric acid in a vacuum, gets solid. The solid product is insoluble in water, and crystallizes from acetic ether in needles melting at 143°; this is probably a polymer, whereas the oily substance is a hydrate,



$$\begin{array}{l} C_6H_5{-}C\begin{smallmatrix}OH\\OH\end{smallmatrix} \\ \qquad\;\; | \\ CH_3N{=}COH. \end{array}$$

The substance shows thus in its behavior great resemblance to benzoylformic-amide, which Claisen has shown* exists in two modifications (probably polymeric), and also forms a low melting hydrate.†

Benzoylformic-methylamide-phenylhydrazonhydrate,



$$\begin{array}{l} CH_3N:COH \\ \qquad\quad | \\ C_6H_5\,.\,C\begin{smallmatrix}OH\\NHNHC_6H_5.\end{smallmatrix} \end{array}$$

On treating benzoylformic-methylamide in concentrated ethereal solution at 0° with an ethereal solution of phenylhydrazine (one molecule), a white voluminous precipitate separates out in flakes, which, after being well washed with ether, dried on a clay plate and a short time over sulphuric acid in a vacuum, was directly analyzed.

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* Ber. d. chem. Ges., XII. 633.

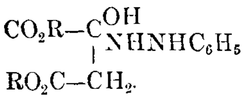
† Ann. Chem. (Liebig), CCLXX. 295, 300, 316.

0.2056 gram substance gave 0.5037 gram CO_2 and 0.1202 gram H_2O.
0.1551 gram substance gave 20.5 c.cm. N_2 at 6° and 745 mm.

	Theory for $C_{15}H_{17}N_3O_2$	Found.
C	66.42	66.77
H	6.27	6.49
N	15.50	15.78

Phenylhydrazine has thus simply added itself to the carbonyl group present in benzoylformicmethylamide, giving rise to a hydrazonehydrate. It is insoluble in water, and is not split into its components by cold sodic hydrate, but possesses a great tendency to lose water, becoming thereby yellow and sticky.

In this connection I would like again to point out that the product which W. Wislicenus* has obtained from oxalacetic ether and phenylhydrazine cannot possibly be a hydrazonehydrate,



$$\begin{array}{l} CO_2R-C\begin{smallmatrix}OH\\ NHNHC_6H_5\end{smallmatrix}\\ \qquad\; | \\ RO_2C-CH_2.\end{array}$$

because it possesses entirely different properties from the hydrazonehydrates obtained by myself,† which under no condition can be split into their components by means of alkalies. The substance obtained by W. Wislicenus shows a totally different behavior; it is, just as phenylhydrazine hydrochloride, a salt-like compound, and is therefore split immediately by alkalies into its components.

Benzoylformic-phenylhydrazone from benzoylformic-methylamide.

That the compounds just described are derivatives of phenylglyoxylic acid is very probable. The pooof of this is furnished as follows: 3 grams benzoylformic-methylamide-phenylhydrazonehydrate are warmed on a water bath for half an hour with 80 c.cm. dilute ten per cent sodic hydrate (the hydrazonehydrate dissolves readily on gentle warming). A strong smell of methylamine is noticed, and on adding dilute hydrochloric acid a yellow flaky precipitate (1.4 grams) comes down, which is dissolved again in soda and reprecipitated by acids. The method of purification used by Elbers [*] does not yield an absolutely pure product; it is much better to recrystallize from benzene, wherein the substance is readily soluble on heating, but practically insoluble in the cold. Yellow needles melting at 163° (Elbers gives mpt. 153°) were thus obtained.

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* Ber. d. chem. Ges., XXIV. 3007

† Ann. Chem. (Liebig), CCLXX. 292, 300, 319, 333.

0.1661 gram substance, dried at 90°, gave 0.4259 gram CO_2 and 0.0750 gram H_2O.

0.1008 gram substance, dried at 90°, gave 11 c.cm. N_2 at 25° and 739 mm.

	Theory for $C_{14}H_{12}N_2O_2$.	Found.
C	70.00	69.93
H	5.00	5.02
N	11.66	11.82

Molecular Rearrangement of Ethylisocyanide to Propionitrile.

Ethylisocyanide was made according to the method of Gautier,[†] by heating 100 grams silvercyanide and 115 grams ethyliodide for one and one half hours on a water bath (with reversed condenser and with a mercury valve). The substance (bpt. 79°) can be kept for fifteen months without the slightest change. It can be heated without any essential change for many hours to 210°; a slight yellow coloration only is noticed.[‡] The first statements of Gautier [§] concerning this substance, which he does not mention in his later paper,[||] are therefore to be corrected. On heating ethylisocyanide, however, to a still higher temperature, molecular rearrangement to ethylcyanide takes place almost quantitatively. 7.5 c.cm. ethylisocyanide are heated in a sealed tube for three hours between 230°–255°, and the contents of the tube, which are colored brown and smell slightly of ammonia and isocyanide, distilled off. Everything came over except a slight residue between 94° and 98°. In order to remove ammonia and traces of isonitrile, the oil was washed with a chloride of calcium solution containing hydrochloric acid, and then dried with solid calcic chloride. On distilling, a pleasant ethereal smelling oil, boiling constant at 97°, was obtained (4 c.cm.), which was identical in every respect with propionitrile.

0.1528 gram substance gave 0.3668 gram CO_2 and 0.1278 gram H_2O.
0.1530 gram substance gave 33.5 c.cm. N_2 at 9° and 741 mm.

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[*] Ann. Chem. (Liebig), CCXXVII. 341.

[†] *Loc. cit.*, [4.], XVII. 233.

[‡] Comptes Rendus, LXV. 862.

[§] *Loc. cit.*, [4.], XVII. 236.

[||] Ibid., 203–260.

	Theory for C_3H_5N.	Found.
C	65.45	65.46
H	9.09	9.29
N	25.45	25.66

The Action of Sulphur on Ethylisocyanide.

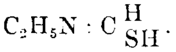
7.5 c.cm. ethylisocyanide, 3.1 grams crystallized sulphur, and 15 c.cm. carbonbisulphide were heated in a sealed tube at 110°–120° for two hours. The reaction is complete, and the mustard oil formed is driven over with steam, extracted with ether, and, after drying with calcic chloride, is fractionated. It boils constant at 131°, and is identical with ethyl-mustard oil first isolated by Hofmann.*

0.2040 gram burnt with lead chromate gave 0.3063 gram CO_2 and 0.1016 gram H_2O.

0.2544 gram substance gave 0.6771 gram $BaSO_4$ (Carius).

	Theory for C_2H_5NCS.	Found.
C	41.38	40.95
H	5.75	5.50
S	36.78	36.55

The Action of Hydrogen Sulphide on Ethylisocyanide.

Thioformethylamide,  $C_2H_5N : C\begin{smallmatrix} H \\ SH \end{smallmatrix}$. 10 c.cm. ethylisocyanide were dissolved in 200 c.cm. absolute alcohol, saturated at 0° with hydrogen sulphide, and then heated for 4 hours in a sealed tube at 100°. The isonitrile smell was entirely gone, and, after distilling off the alcohol, the brown oily residue was fractionated under reduced pressure. The chief portion boiled at 140°–150° at 40 mm. pressure, and, on the second distillation, a yellow oil, smelling of sulphur, and boiling at 125° at 14 mm. pressure was obtained.

0.1996 gram substance, burnt with lead chromate, gave 0.2980 gram CO_2 and 0.1468 gram H_2O.

0.2034 gram substance, gave 29.5 c.cm. N_2 at 18° and 737 mm.

0.2885 gram substance gave 0.7529 gram $BaSO_4$ (Carius).

	Theory for C_3H_7NS	Found.
C	40.45	40.71
H	7.87	8.17
N	15.73	16.23
S	35.95	35.84

---

* Ber. d. chem. Ges., I. 26.

Ethylisocyanchloride or Ethylimidocarbonylchloride, $C_2H_5N=CCl_2$.

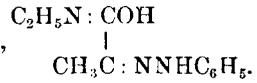
On passing dry chlorine over a solution of 10 c.cm. ethylisocyanide in 40 c.cm. chloroform, the gas is absorbed instantly, without the slightest trace of hydrochloric acid or of coloration being noticeable. As soon as the solution is colored yellow, or smells of chlorine, it is directly fractionated. It was possible to obtain a small amount of a colorless, very sharp-smelling oil, boiling at 99°-100°. Since, however, the separation from the large amount of chloroform can only be accomplished with much loss of material, the ethylisocyanchloride is better prepared as follows: 5 c.cm. ethylisocyanide, diluted with four times its volume of absolute ether, are cooled to —15° and 5.5 c.cm. sulphurylchloride are slowly added. An energetic reaction takes place, and the solution becomes colored yellow and smells strongly of sulphurdioxide. After ten minutes' standing, the solution is washed with dilute sodic hydrate, and then dried with calcic chloride. On fractionating, a colorless, intensely sharp-smelling oil, boiling at 102°, is obtained.

0.2994 gram substance gave 0.3183 gram CO_2 and 0.1101 gram H_2O.
0.2450 gram substance gave 0.5536 gram AgCl (Carius).
0.1575 gram substance gave 14.5 c.cm. N_2 at 8° and 745 mm.

	Theory for $C_3H_5NCl_2$.	Found.
C	28.57	28.99
H	3.97	4.09
N	11.11	10.90
Cl	56.35	55.90

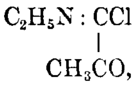
The Action of Acetylchloride on Ethylisocyanide.

Pyruvic-ethylamide-phenylhydrazone,



$$\begin{array}{l} C_2H_5N:COH \\ \quad | \\ CH_3C:NNHC_6H_5. \end{array}$$

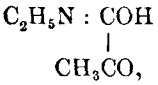
Ethylisocyanide (7.5 c.cm.) and acetylchloride (6.5 c.cm., one molecule) react on each other when mixed together readily at 0°, and the solution becomes colored yellow. After standing for twelve hours at ordinary temperature, a dark brown liquid is obtained, which was divided into two portions, *a* and *b*. On fractionating *a*, it all distilled over between 50° and 60° at 15 mm. pressure, as a yellow oil which, redistilled at ordinary pressure, boils at 100°–130°. In both cases the oil smells of isonitrile, so that a dissociation of the ethylimidopyruvylchloride,



$$\begin{array}{r} C_2H_5N:CCl \\ | \;\; \\ CH_3CO, \end{array}$$

into its components must take place on distillation, and an analysis of the substance would therefore be of no value. One encounters here, as has also been observed in the case of many other addition products of the isocyanides,* the remarkable property that these are easily split into their components, either at higher temperatures, or on standing in the cold, or on treatment with sodic hydrate; whereas, on the other hand, these components either at —20° or at ordinary or higher temperatures often unite with explosive violence. *Bivalent carbon therefore behaves exactly like trivalent nitrogen* in ammonia and the amines, since also the last named compounds unite often with explosive violence with acids, e. g. hydrochloric acid, forming addition products containing quinquivalent nitrogen, which in turn, either by heating or by treating with alkalies, are split into their components.

That the above distilled oil *a*, however, still contains much ethylimidopyruvylchloride, is shown by decomposing it with water: it is converted thereby into pyruvic-ethylamide,



$$\begin{array}{r} C_2H_5N:COH \\ | \;\; \\ CH_3CO, \end{array}$$

the presence of which in the aqueous solution, since it cannot be extracted therefrom by ether, is best shown by adding phenylhydrazinehydrochloride, which precipitates an insoluble hydrazone (3.5 grams).

The above mentioned portion *b* was not distilled, but decomposed directly with ice water, and the reddish-colored solution treated with phenylhydrazinehydrochloride, and thus 7.7 grams insoluble hydrazone were obtained. The hydrazone is obtained, when recrystallized from alcohol, in colorless many-sided heavy crystals, melting at 165°. It is insoluble in alkalies and in water.

0.2002 gram substance, dried at 100°, gave 0.4731 gram CO_2 and 0.1387 gram H_2O.

0.1494 gram substance, dried at 100°, gave 27.5 c.cm. N_2 at 20° and 747 mm.

	Theory for $C_{11}H_{15}N_3O$.	Found.
C	64.39	64.44
H	7.31	7.69
N	20.49	20.69

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* Ann. Chem. (Liebig), CCLXX. 297, 298, 322.

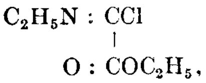
The Action of Phosgene on Ethylisocyanide.

On adding slowly 5 c.cm. phosgene (cooled to —15°) to 10 c.cm. ethylisocyanide (cooled to —19°), reaction takes place always with explosive violence. Even when the isocyanide is diluted with an equal volume of absolute ether and the solution is cooled to —19°, a very energetic union takes place on adding the phosgene, which makes it difficult to regulate the reaction. A yellow sharp-smelling liquid is formed, which does not boil without decomposition. On pouring it into water a brown solution containing much hydrochloric acid is formed, from which ether extracts nothing, and which gives no precipitate with phenylhydrazine. The products, which are in all probability all derivatives of mesoxalic acid,* were not further investigated.

The Action of Chlorocarbonic Ether on Ethylisocyanide.

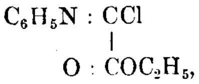
An addition of chlorocarbonic ether, or of alkyliodides or chlorides, to aromatic derivatives of isocyanogen could not be accomplished, because a reaction takes place only at high temperatures, and this must result in the formation of much resinous polymeric products, as well as in the decomposition of the addition products first formed.†

An addition of chlorocarbonic ether to ethylisocyanide has, however, been accomplished, and with the following experiences. Chlorocarbonic ether reacts, already, at ordinary temperatures, on ethylisocyanide and the mixture becomes colored yellow. On heating at 100°, complete reaction takes place in a very short time, but the addition product first formed,



$$\begin{array}{rl} C_2H_5N : & CCl \\ & | \\ O : & COC_2H_5, \end{array}$$

is completely split into carbondioxide, ethylchloride, and ethylisocyanide, $C_2H_5N : C$, which, generated in the nascent state, mostly polymerizes. Klinger has already observed an entirely analogous decomposition in the case of oxanilethane-imidechloride,



$$\begin{array}{rl} C_6H_5N : & CCl \\ & | \\ O : & COC_2H_5, \end{array}$$

on heating it to 120°.‡

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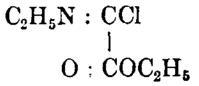
* Ann. Chem. (Liebig), CCLXX. 286–295 and 315.

† Ibid., CCLXX. 280, *et seq.* Cf. also Wallach, Ibid., CLXXXIV. 86, 108, CCXIV. 283.

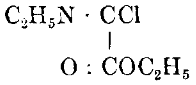
‡ Ibid., CLXXXIV. 283.

That in the above case an intermediate formation of the imidechloride



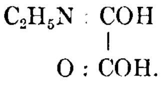
$$\begin{array}{r@{\;}l} C_2H_5N : & CCl \\ & | \\ O : & COC_2H_5 \end{array}$$

takes place was proved as follows. 5 c.cm. ethylisocyanide and 7.8 grams chlorocarbonic ether were heated for 6 hours at 60°–70°, whereby a copious evolution of carbondioxide and of ethylchloride takes place. The very dark residue was treated with absolute ether and much polymerized ethylisocyanide separated out in brown flakes The ethereal filtrate gave a small amount of an oil (free from chlorocarbonic ether), which was warmed gently with lime water. After getting rid of the excess of lime by means of carbonic acid, the filtrate gave, on concentration, crystals of calcic ethyloxaminate, which separated out in needles. The free ethyloxaminic acid obtained from this salt melted at 123°, and was found identical in its properties (as well as also the salt) with the previous statements of Wallach.* The yield of calcic ethyloxaminate is very poor, — never over 0.2 gram; its source can only be explained through the intermediate formation of the imidechloride



$$\begin{array}{r@{\;}l} C_2H_5N \cdot & CCl \\ & | \\ O : & COC_2H_5 \end{array}$$

in the above reaction this substance must necessarily, by saponification, yield ethyloxaminic acid,



$$\begin{array}{r@{\;}l} C_2H_5N : & COH \\ & | \\ O : & COH. \end{array}$$

A better yield of the imidechloride could, in all probability, be expected on allowing molecular proportions of ethylisocyanide and chlorocarbonic ether to stand at ordinary temperature for a week or more.

From the above experiments, it is clear that the aliphatic isocyanogen derivatives behave in a manner entirely analogous to the corresponding aromatic derivatives, and differ from these only in the fact that they react more energetically. It was further shown that carbon tetrachloride reacts with ethylisocyanide at 180°, benzolsulphochloride at 85°, benzylchloride at 120°; it was not possible, however, to isolate any definite addition products.

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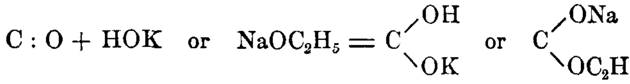
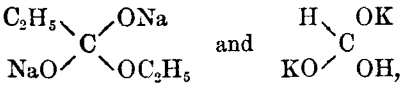
* Ann. Chem (Liebig), CLXXXIV. 58.

It is a noteworthy fact that ethylisocyanide can be heated in a sealed tube for one hour to a temperature of 130°–170° with sodium ethylate (free from alcohol) without the slightest change. For this reason, it seems to me that in the action of caustic potash or sodium ethylate * on the inert carbonic oxide,† an addition of these reagents to the carbonylgroup ‡ must first take place, as follows:



The bivalent carbon atom present in these addition products must, according to the ideas heretofore developed in these Proceedings,§ be far more reactive than the unsaturated carbon atom present in the isocyanides; and, in consequence, a further addition of sodic ethylate or of caustic potash takes place, giving rise to the ortho derivatives,



which naturally, on treatment with water, go over into propionic acid and formic acid salts, respectively.

II. Fulminic Acid is identical with Carbyloxime, and contains Bivalent Carbon, $C:NOH$.

Formylchloridoxime, $HON:C{}^{H}_{Cl}$. The synthesis of fulminate of mercury from sodic nitromethane, described in the preceding paper, leads directly to the conclusion that this substance must be identical with mercuric carbyloxime, $C:NOhg$. The behavior of the salt towards concentrated hydrochloric acid is also in favor of this conclusion; there is formed, as Steiner,|| Carstanjen and Ehrenberg,¶ and especially also Divers and Kawakita,** have shown, not a trace of oxalic acid, but only formic acid, corrosive sublimate, and hydroxylamine hydrochloride.

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* Berthelot, Ann. Chem. (Liebig), XCVII. 125; Geuther and Fröhlich, Ann. Chem. (Liebig), CCII. 290.

† Ann. Chem. (Liebig), CCLXX. 267.

‡ Ibid., CCLXX. 322.

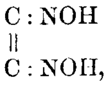
§ Vol. XXVII. pp. 102–104.

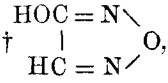
|| Ber. de. chem. Ges., XVI. 1484, 2419

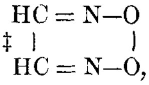
¶ Journ. f. prakt. Chem., [2.], XXV. 232; XXX. 38.

** Journ. chem. Soc., XLV. 13–30, 75.

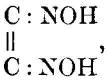
Notwithstanding this, all the formulæ yet proposed for fulminic acid, as, for example, that of

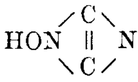
Steiner,[*] 

$\begin{matrix}C:NOH\\ \|\\ C:NOH\end{matrix}$, of Divers,[†] 

, of Scholl,[‡] 

and many others, have originated from the assumption that this substance contains two carbon atoms in the molecule, because it was regarded as proved by the experiments of Liebig and Gay-Lussac[§] that the fulminic acid molecule contains two hydrogen atoms possessing entirely different functions. The behavior of mercury fulminate towards bromine[||] and towards iodine,[¶] whereby products are formed which unquestionably contain two carbon atoms in the molecule, as well as the decomposition of this salt, by means of chlorine, into cyanogen chloride and chlorpicrine,[**] seem also to be in favor of this conclusion. Only very recently has Scholl[††] thought of the possibility of the simple carbyloxime formula, $C:NOH$, but he still gives the polymerized formula of Steiner,



$\begin{matrix}C:NOH\\ \|\\ C:NOH\end{matrix}$, or  NOH, the preference.[‡‡]

I have succeeded in proving experimentally, with absolute precision, that fulminic acid is identical with carbyloxime, $C:NOH$, and that the bivalent carbon atom present in this substance possesses a most surprising and enormous reactivity, so that in all reactions shown by fulminic acid salts the unsaturated carbon atom is the point of attack; and, since we now possess some light on the nature of bivalent carbon, the entire chemistry of the fulminic acid derivatives is very simply and completely explained, as will become evident from the following experiments.

It has for over seventy years been considered as settled that, on treating fulminic acid salts with dilute hydrochloric acid, a complete destruction of the fulminic acid molecule takes place, and that among other products prussic acid is set free: this observation has repeatedly been confirmed. *Not a trace of prussic acid is formed, however, but formylchloridoxime,* $\mathrm{HON : C}^{\mathrm{H}}_{\mathrm{Cl}}$, a substance which, in dilute aqueous solution, — probably because of a slight dissociation into hydrochloric acid and carbyloxim, $\mathrm{C : NOH}$, — has an odor which cannot be distinguished from that of prussic acid.

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[*] Ber. d. chem. Ges., XVI. 1484, 2419.

[†] Journ. chem. Soc., XLV. 21.

[‡] Ber. de chem. Ges., XXIII. 3497, 3507.

[§] Annales de Chim. et de Phys., XXIV. 294–317, XXV. 285–310.

[||] Kekulé, Ann. Chem. (Liebig), CV. 280.

[¶] Sell and Biedermann, Ber. d. chem. Ges., V 89.

[**] Kekulé, Ann. Chem. (Liebig), CI. 206

[††] Ber. d. chem. Ges., XXIII. 3506–3509.

[‡‡] Ber. d. chem. Ges., XXIV. 581.

This is the reason why, among others,* Liebig and Gay-Lussac, as well as Schischkoff, state that prussic acid is formed in this treatment although, as they themselves add, the presence of prussic acid could not be proved. Gay-Lussac and Liebig write: † "Dans l'intention d'obtenir quelques lumières à cet égard, nous avons essayé d'évaluer la quantité d'acide hydrocyanique qui se dégage lorsqu'on traite le fulminate d'argent par l'acide hydrochlorique, etc. Nous espérions obtenir du cyanur d'argent; mais, à notre grande surprise, il ne s'est fait aucune précipitation, quoique nous nous fussions assurés que la même dissolution d'argent donnait un abondant précipité lorsqu'on y versait de l'acide hydrocyanique."

Schischkoff says: ‡ "Für das Knallsilber war bereits beobachtet, dass es bei der Einwirkung von Chlorwasserstoffsaüre Cyanwasserstoff entwickelt; ich versuchte dieselbe Reaktion mit Knallquecksilber, und war zuerst sehr erstaunt, dass ich nicht ein analoges Resultat nachweisen konnte. Ich schrieb dieses abweichende Verhalten dem Umstande zu, dass sich, in letzterem Falle, ein Quecksilberverbindung von unbekannter Natur bilden möge, welche den Cyanwasserstoff zurückhalten möge. Und, in der That, wenn man vorher etwas schwefelsaures Eisenoxydul der Chlorwasserstoffsäure zusetzt, so lässt sich leicht eine reichliche Entwicklung von Cyanwasserstoff constatiren. Durch das zugesetzte Eisenoxydulsalz wird vermuthlich die den Cyanwasserstoff gebunden zurückhaltende Verbindung zersetzt."

Formation of Formylchloridoxime from Sodic Fulminate. — The fulminate of mercury used in these experiments was made according to the method of Lobry de Bruyn; § 32 grams of dry salt were regularly obtained from 25 grams of mercury used. Carstanjen and Ehrenberg were the first to show that this salt can be converted quantitatively into sodic fulminate by means of sodium amalgam.* It is possible to convert 32 grams of mercury fulminate in 20 minutes into an aqueous colorless solution of sodic fulminate (free from mercury) as follows. The salt is suspended in about 125 c.cm. water and treated with 75 grams of 8 per cent sodium amalgam,† (5 grams more than the theory). The operation is first carried out in a flask, cooling well with water, and then in a flask, having a well fitting glass stopper, taking care to shake thoroughly until the solution contains no mercury.

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* Cf. Ehrenberg, Journ. f. prakt. Chem., [2.], XXV. 241; Scholvien, Ibid., XXXII. 463.

† Annales de Chim. et de Phys., XXV 308.

‡ Ann. Chem. (Liebig), Suppl. Vol., I. 108

§ Ber. de chem. Ges., XIX. 1370.

The sodium fulminate solution thus obtained (about 150 c.cm.) is cooled to 0°, and added slowly, taking care to cool well, to a solution of hydrochloric acid at 0° (114 parts concentrated acid 1.18, and 114 parts water) and thereupon extracting immediately three times with ether. The ethereal solution is placed in a distilling flask and concentrated to one third its volume by distilling off the ether in a stream of dry air at a low temperature (40°), and the solution is then concentrated further at reduced pressure. A very concentrated solution of formylchloridoxime in ether is thus obtained, from which the pure substance is isolated by pouring on a watch-glass and evaporating rapidly in a vacuum desiccator. To insure success in these operations, a very cold winter temperature is essential, and the concentrated ethereal solutions must be kept at 0°. On evaporation of the ether, perfectly transparent very long colorless needles, clear as glass, separate out, which are first transferred to a clay plate (cooled at 0°) and quickly powdered with a platinum spatula, and then weighed as quickly as possible at a low temperature.

0.1235 gram substance, poured directly after weighing into water, and treated with silver nitrate and concentrated nitric acid, gave, after digesting on a water bath, 0.2128 gram AgCl.

0.6585 gram substance gave 1.1006 grams AgCl.

	Theory for CH_2NOCl.	Found.	
Cl	44.65	42.63	41.35

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* Journ. f. prakt. Chem., [2.], XXV. 241. Cf. also Scholvien, Ibid., XXXII. 462.

† Sodium amalgam is best made by adding 80 grams sodium to 400 c.cm. toluene in a two-litre flask, and then slowly adding 920 grams of mercury. The toluene heats up to its boiling point, and, after about one half of the mercury has been added, the mass gets solid. The toluene is poured off, the residue melted in a crucible, and then poured out on clay plates. In this way large quantities of sodium amalgam can be made without danger, and with the greatest ease. Cf. Chem. Zeit., 1864, p. 720, and Gmelin, Kraut, III. 857.

Preparation of Formylchloridoxime from Silver Fulminate. — Fulminate of silver is best obtained as follows. 5 grams of silver are dissolved in 100 grams nitric acid (sp. gr. 1.34), and the warm solution is poured into 150 c.cm. alcohol (90 per cent) and then heated for 5 to 10 minutes on a water bath until a reaction sets in. The reaction then continues very energetically, of its own accord, and silver fulminate separates out in beautiful needles. The yield is regularly 6.5 grams or more, and the filtrate contains only traces of silver. The salt is much less soluble in boiling water than Liebig states.* In the dry state it is far more dangerous than the mercury salt: it explodes instantly, and with tremendous violence, on touching it very carefully with a platinum spatula. It can, however, be dried without the slightest danger on filter paper, and collected therefrom by means of a camel's hair brush. A silver determination of the salt, dried over sulphuric acid in a vacuum, gave the following result.

0.2013 gram substance, digested with dilute hydrochloric and nitric acids, gave 0.1925 gram AgCl.

	Theory for AgONC.	Found.
Ag	72.00	71.92

In order to convert silver fulminate into formylchloridoxime, 12 grams salt are added to 80 c.cm. hydrochloric acid (one part concentrated acid to one part water) containing pieces of ice, and then, after decanting or filtering from the chloride of silver, proceeding as above in the case of the sodium salt. A small portion of the concentrated ethereal solution of formylchloridoxime was evaporated as above, and the substance immediately analyzed: the chief portion was treated directly with 12.5 grams of aniline (2 molecules) and thus converted smoothly into phenylisuretine (see below).

0.4478 gram substance gave 0.7758 gram AgCl.

	Theory for CH_2NOCl.	Found.
Cl	44.65	42.68

Properties of Formylchloridoxime. — The formylchloridoxime obtained in these two ways is a very reactive and remarkable substance. In the solid condition, or in concentrated ethereal solution, it can be kept at 0° for some time unchanged. It volatilizes very quickly and completely, in small portions, at ordinary temperature, and this serves as a good means of determining its purity. It often happens, when all possible precautions in its manufacture are not observed, that a product is obtained which is only partially volatile, and leaves an amorphous opaque residue. This can, however, be seen immediately by the appearance of the formylchloridoxime itself when prepared; if the crystals are clear as glass, the substance is pure; if, on the other hand, the crystals are turbid or opaque, the product is impure. In larger amounts (a few decigrams) formylchloridoxime decomposes very soon at ordinary temperature; it at first becomes colored green, and then puffs up with tremendous evolution of heat and a hissing noise. The same decomposition takes place instantly by the heat of the hand, or on heating the substance in a vacuum at 40°. Carbon monoxide is given off and the puffed up sticky residue consists chiefly of hydroxylamine hydrochloride.

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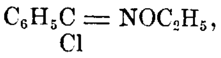
* Annales de Chim. et de Phys., XXIV 297.

The substance thus possesses a tremendous tendency to decompose into hydrogen chloride and carbyloxime, $C:NOH$, and the latter compound is then split by the hydrochloric acid into carbonmonoxide and hydroxylamine. Formylchloridoxime possesses very poisonous properties, has a very sharp pungent smell, and diluted with air or in dilute aqueous solution has an odor which cannot be distinguished from that of prussic acid; this is probably due to a partial dissociation into hydrogen chloride and carbyloxime, $C:NOH$. Also the action of the substance on the human system, producing a flow of saliva, an irritation in the throat, and violent headaches, is entirely analogous to that of prussic acid. Formylchloridoxime possesses also a very sharp pungent smell, and acts violently on the eyes; the action is not at first very noticeable, but sets in after a time. Thus, for example, after being exposed to the influence of the vapor of the substance for about one hour on an afternoon, my eyes were only colored intensely red, but in the evening a most violent inflammation set in, so that I could hardly see for twenty-four hours. The consequences, however, are only temporary.

Formylchloridoxime, when brought on the skin, causes white blisters and deep wounds, which heal only very slowly. The substance is not decomposed either by water or by alcohol, — a noteworthy property for a soluble acid chloride; in this respect it resembles the acid chloride, benzenylethoximchloride,



$$\underset{\textstyle Cl}{C_6H_5C} = NOC_2H_5,$$

obtained by Tiemann and Krüger,* which is stable even towards caustic potash. The constitution of the substance as formylchloridoxime,

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* Ber. d. chem. Ges., XVIII. 732.

$$HON : C^{H}_{Cl},$$

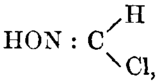
is proved by its behavior towards silver nitrate, ammonia, and especially towards aniline.

Behavior of Formylchloridoxime towards Silver Nitrate.

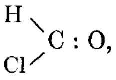
Synthesis of Silver Fulminate, C : NOAg. — On treating an aqueous solution of formylchloridoxime with two molecules of silver nitrate, a quantitative interaction takes place, forming silver fulminate and chloride of silver according to the equation:

$$HON : C^{H}_{Cl} + 2\ AgNO_3 = C : NOAg + AgCl + 2\ HNO_3.$$

This shows what a great tendency exists in this formic acid derivative to split off hydrogen chloride and generate carbyloxime, C : NOH. Some analogous facts to show that this same tendency exists, have already been presented in the previous paper:[*] whereas the oxime of formylchloride,



can be isolated, formylchloride itself,



does not exist even at 0°, but decomposes spontaneously into hydrogen chloride and into carbon monoxide.

The separation of the chloride of silver and silver fulminate formed in the above reaction can be accomplished very readily. The precipitate, after some standing, and addition of cold dilute nitric acid, is filtered off, well washed, and then boiled out three times with small quantities of aqueous potassic chloride. On cooling, or on concentrating the filtrates, the double salt, AgONC, KONC, discovered by Liebig,[†] separates out in long glistening flat needles. This salt, after recrystallizing from water, is dissolved in warm water and poured into an excess of cold dilute nitric acid, whereby regenerated silver fulminate comes down in very fine colorless needles. Liebig and Gay-Lussac[*] have regarded this precipitate as "acide fulminique," $C_2HAgN_2O_2$, which is incorrect.

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[*] Ann. Chem. (Liebig), CCLXX. 307, 308, 322.

[†] Annales de Chim. et de Phys., XXIV. 315.

0.2097 gram substance, dried over H_2SO_4 in a vacuum, gave 0.1988 gram AgCl.

	Theory for AgONC.	Found.
Ag	72.00	71.37

That silver fulminate, and not "acide fulminique," $C_2HAgN_2O_2$, is always formed on treating the double salt AgONC, KONC, with nitric acid, was further proved by making the double salt from silver fulminate (made in the ordinary way from silver, nitric acid, and alcohol), and treating it as above, with nitric acid.

0.2129 gram substance, dried over H_2SO_4 in a vacuum, gave 0.2031 gram AgCl.

	Theory for AgONC.	Found.
Ag	72.00	71.80

The conclusion of Liebig and Gay-Lussac that the fulminic acid molecule contains two hydrogen atoms, possessing entirely different functions, is therefore not justifiable. In exactly the same way as cyanide of potash gives with silver cyanide a soluble double salt, AgN : C, KN : C, the entirely analogously constituted silver fulminate gives with potassic fulminate a corresponding double salt, AgON : C, KON : C. The analogy between the salts of fulminic acid and those of prussic acid is altogether a surprisingly close one, — which can now hardly be considered strange, because both these acids are quite analogous derivatives of isocyanogen. It will be shown further on that a double salt, sodium ferrofulminate, $Na_4Fe\,(ON : C)_6$, exists, corresponding thus in every respect to the yellow prussiate of soda, sodic ferrocyanide, $Na_4Fe\,(N : C)_6$. The physiological properties of the soluble prussic acid salts, MN : C, and those of the soluble fulminic acid salts, MON : C, are so much alike that it is impossible, as far as we now know, to distinguish between them. Schischkoff is only one of the many observers who have worked with salts of fulminic acid who observed the poisonous properties of these salts (the enormous explosive properties are mentioned by all). He remarks:[†] "Die Knallsäuresalze sind ganz so giftig wie die Cyanmetalle. Die Heftigkeit der Wirkung hängt von der Löslichkeit ab, aber

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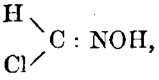
[*] Annales de Chim. et de Phys., XXIV. 302, XXV. 289.

[†] Ann. Chem. (Liebig), Suppl. Vol., I. 109.

die Vergiftungssymptome sind ganz dieselben wie sie durch die Cyanmetalle hervorgebracht werden. So ist das Knallzink, welches eines der löslichsten unter den Knallsäuresalzen ist, zugleich das giftigste. Ich bemerke noch dass die isocyanursauren Salze [die Fulminurate] gar nicht giftig sind."

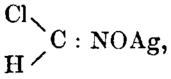
E. Davy[*] first obtained zinc fulminate from mercury fulminate by means of zinc dust and water, and made therefrom, by double decomposition with the metallic hydroxides, many salts of the alkali and alkaline-earth metals. That the majority of these salts are not simple but double salts, e. g. that Davy's baric fulminate is a zinc barium fulminate, baON : C, znON : C, was first shown by Fehling.[†] Ehrenberg is the first who obtained sodic fulminate pure and analyzed the product.[‡]

Other Syntheses of Silver Fulminate. — The behavior of silver fulminate towards the calculated amount (one molecule) of dilute hydrogen chloride and of hydrogen sulphide is very remarkable, and is fully cleared up by what follows. On adding one molecule of dilute hydrogen chloride to silver fulminate, suspended in water and kept cold by means of pieces of ice, an energetic reaction immediately takes place, and a strong smell of formylchloridoxime is noticed. The mixture is well stirred, and as soon as it can be filtered clear, this is done. The perfectly clear filtrate is found to contain two substances, formylchloridoxime,



$$\begin{array}{l}H\diagdown\\ \qquad C : NOH,\\ Cl\diagup\end{array}$$

which can easily be extracted from the solution by means of ether, and silver formylchloridoxime,



$$\begin{array}{l}Cl\diagdown\\ \qquad C : NOAg,\\ H\diagup\end{array}$$

which is soluble in water. The solution, therefore, contains *much chlorine and silver,* which for a long time seemed very enigmatic: on addition of hydrochloric acid, silver chloride is precipitated, and on addition of nitric acid a precipitate consisting of silver fulminate and silver chloride is formed.

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[*] Trans. Roy. Soc. Dublin, 1829; extract in Berzelius's Jahr., XII. 97, 120.

[†] Ann. Chem. (Liebig), XXVII. 30.

[‡] Journ. f. prakt. Chem., [2.], XXXII. 231.

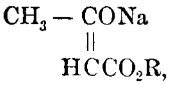
It follows from the above that on treating silver fulminate with dilute hydrochloric acid (one molecule) an addition of hydrogen chloride to the unsaturated carbon atom in this salt takes place,

$$AgON : C + HCl = AgON : C^{H}_{Cl} .$$

The addition product, which is soluble in water, is then, in the second stage of the reaction, further acted upon by some of the hydrogen chloride present, and converted partially into silver chloride and formylchloridoxime,

$$AgON : C^{H}_{Cl} + HCl = HON : C^{H}_{Cl} + AgCl.$$

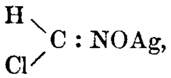
This experiment demonstrates, therefore, in a very pretty manner, that an organic silver salt can react with hydrogen chloride, *leaving the silver present in the molecule entirely intact.* The bivalent carbon atom present in fulminate of silver is so reactive, that the metal is not affected at all. I have already repeatedly, in other cases, drawn attention to similar reactions: the double bond present in sodium acetacetic ether,



$$\begin{array}{l} CH_3 - CONa \\ \qquad\quad \| \\ \qquad\quad HCCO_2R, \end{array}$$

is so reactive that, on treatment of this salt with alkyliodides and acid chlorides,* exclusively or chiefly an addition of these reagents to the double bond takes place, and the sodium atom remains entirely intact in the whole reaction. The same phenomenon has also already been proved to take place with many other silver salts.†

The isolation of the intermediate product,



in the above instance therefore furnishes a further very important experimental confirmation of the processes which I have shown take place in the interaction of acetacetic salts with alkyliodides and acid chlorides. A further entirely analogous example of addition is furnished by the study of the action of hydrogen sulphide on silver fulminate. On adding to silver fulminate, suspended in water containing pieces of ice, an aqueous solution of hydrogen sulphide (one molecule), reaction sets in immediately, and a strong odor resembling very closely that of prussic acid is noticed. The clear colorless filtrate contains both *silver and sulphur;* on addition of silver nitrate, a brown precipitate consisting of silver fulminate and silver sulphide is obtained; hydrochloric acid precipitates chloride and sulphide of silver. On treating silver fulminate with hydrogen sulphide, an addition must therefore take place as follows:

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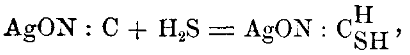
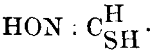
* Ann. Chem. (Liebig), CCLXVI. 52, CCLXX. 331, CCLXXVI. 200.

† Ann. Chem. (Liebig), CCLXX. 329, CCLXXVI. 234, CCLXXVII. 73 Cf. also page 147 of the preceding paper.



$$AgON : C + H_2S = AgON : C^{H}_{SH},$$

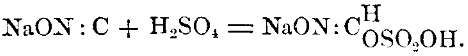
forming silver thioformhydroxamate, which, like silver formylchloridoxime, is soluble in water; this salt is then further acted upon by hydrogen sulphide, and partially converted into silver sulphide and thioformhydroxamic acid,



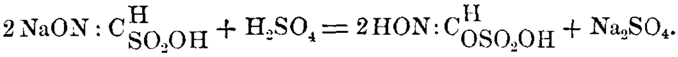
$$HON : C^{H}_{SH}.$$

The above facts suffice also to explain fully the former experiments of Ehrenberg[*] and of Scholvien.[†] Scholvien believed he had obtained free fulminic acid on adding aqueous sodic fulminate to cold dilute sulphuric acid and extracting *immediately* with ether, for he obtained by shaking the ethereal solution quickly with silver nitrate a precipitate of silver fulminate.[‡] He describes the "free fulminic acid" as a volatile compound, which affects the eyes and mucous membrane of the nose in an intolerable manner.

It is now clear that Scholvien's compound was nothing else than formylsulphate-oxime, $HON:C^{H}_{OSO_2OH}$, formed by an addition of sulphuric acid to the unsaturated carbon atom present in sodic fulminate, as follows:



$$NaON:C + H_2SO_4 = NaON:C^{H}_{OSO_2OH}. \qquad (I.)$$



$$2\,NaON:C^{H}_{SO_2OH} + H_2SO_4 = 2\,HON:C^{H}_{OSO_2OH} + Na_2SO_4. \qquad (II.)$$

Formylsulphate-oxime is a substance which is far less stable than the analogous formylchloridoxime described above, which is not surprising. It possesses, just as formylchloridoxime, only to a far greater extent, a tendency to split into sulphuric acid and carbyloxime, C:NOH. This is the reason why Scholvien always noticed in an ethereal solution of the substance after a few moments a rise in temperature, "which often is so great that the ether begins to boil." * The carbyloxime formed in the nascent state polymerizes to a great extent, just as has often been noticed in analogous cases with isocyanides. For this reason it seems to me highly probable that Scholvien's isocyanuric acid † consists simply of polymerized carbyloxime, and probably possesses the constitution

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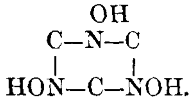
[*] Journ. f. prakt. Chem., [2.], XXX, 43.

[†] Ibid., XXXII. 463, 480.

[‡] Ibid., XXXII., 463, 481.



$$\begin{array}{c} \mathrm{OH} \\ \mathrm{C{-}N{-}C} \\ | \qquad | \\ \mathrm{HON{-}C{-}NOH.} \end{array}$$

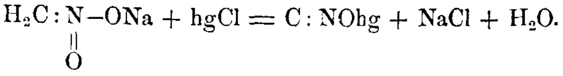
All the properties of the substance can easily be explained by this formula, and a further study of it will be taken up very shortly; especially also because Scholvien states that on treating the silver salt $C_3HN_3O_3Ag_2$ with ethyliodide, "a filtrate was obtained smelling strongly of carbylamine." ‡ It is very likely that in this reaction no ethyl isocyanide, but ethylcarbyloxime, $C_2H_5ON:C$, is formed, — a substance which, as will be shown farther on, cannot be distinguished from ethylisocyanide in respect to odor.

Ehrenberg has already had an ethereal solution of formylchloridoxime (containing also mercuric chloride and hydrogen chloride) in his hands. He obtained it by passing dry hydrogen chloride over mercuric fulminate suspended in absolute ether; and he assumes that free fulminic acid may possibly be present in the solution. He describes the ethereal solution § as a "strong-smelling liquid, bringing tears to the eyes, and affecting the mucous membrane, and causing an intensely bitter taste in the mouth. The smell reminds one of prussic acid, but this could not be detected in the solution. On attempting to distil off the ether, the mass all at once decomposed with violence and with a hissing noise."

Ehrenberg was, in consequence, unable to isolate the product, and studied only the action of aqueous ammonia upon the ethereal solution of the substance. The nature of the compounds which he obtained in this way is cleared up by the experiments mentioned below.

Fulminic acid salts can therefore be obtained synthetically in four different ways, as follows.

1. From sodic nitromethane:



$$H_2C:\underset{\overset{\|}{O}}{N}{-}ONa + hgCl = C:NOhg + NaCl + H_2O.$$

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* Journ. f. prakt. Chem., [2.], XXXII. 463.

† Ibid., XXXII. 464.

‡ Ibid., XXXII. 473.

§ Ibid., XXX. 44

2. From formylchloridoxime:

$$\left.\begin{matrix}H\\Cl\end{matrix}\right\rangle C:NOH + 2AgNO_3 = C:NOAg + AgCl + 2\,HNO_3.$$

3. From formylsulphate-oxime:

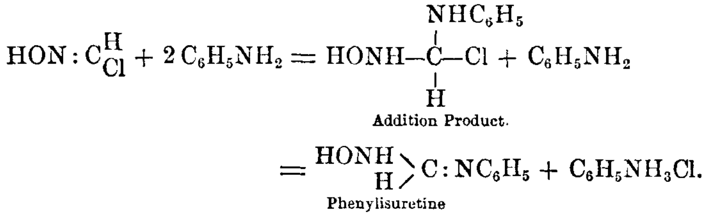
$$HON:C^{H}_{OSO_2OH} + 3AgNO_3 = C:NOAg + Ag_2SO_4 + 3\,HNO_3.$$

4. From thioformhydroxamic acid:

$$HON:C^{H}_{SH} + 3AgNO_3 = C:NOAg + Ag_2S + 3\,HNO_3.$$

Behavior of Formylchloridoxime towards Aniline.

The constitution of formylchloridoxime is proved by the fact that aniline coverts it quantitatively into phenylisuretine, according to the reaction:



$$HON:C^{H}_{Cl} + 2\,C_6H_5NH_2 = \underbrace{HONH{-}\overset{\overset{NHC_6H_5}{|}}{\underset{\underset{H}{|}}{C}}{-}Cl}_{\text{Addition Product.}} + C_6H_5NH_2$$

$$= \underbrace{\left.\begin{matrix}HONH\\H\end{matrix}\right\rangle C:NC_6H_5}_{\text{Phenylisuretine}} + C_6H_5NH_3Cl.$$

On adding an ethereal solution of aniline (2 molecules, 12.5 grams) to a concentrated ethereal solution of formylchloridoxime (obtained from 12 grams silver fulminate), a clear solution at first takes place, but very soon a white salt begins to separate out in large quantity. After standing for one hour, much ether is added, and the salt filtered off. The residue, 9.2 grams, consists of a mixture of aniline hydrochloride and phenylisuretine, which, since the latter substance is insoluble in cold water, can readily be separated. The ethereal filtrate gives, on evaporation, phenylisuretine and traces of aniline. Altogether 6.5 grams of phenylisuretine were obtained. It is purified by crystallizing from ether, and obtained in flat colorless needles, melting with decomposition at 138°. The substance crystallizes from water in long fibrous colorless needles, or, if the solution is dilute, in leaflets. A slight decomposition into phenylisocyanide and hydroxylamine, according to the equation,

$$C_6H_5N:C^{H}_{NHOH} = C_6H_5N:C + H_2NOH,$$

always takes place on recrystallizing the substance from water. Phenylisuretine shows altogether a great tendency to decompose in this manner. On melting the solid substance, a strong smell of phenylisocyanide is noticed; also on warming with sodic hydrate, in which it first dissolves. The compound possesses strong basic properties, and dissolves immediately in cold dilute acids. It gives a deep purple red coloration with ferric chloride, and reduces silver solutions on warming. Because of its decomposition into phenylisocyanide, the substance burns with great difficulty.*

0.1435 gram substance, dried over H_2SO_4 in a vacuum, gave 0.3202 gram CO_2 and 0.0799 gram H_2O.

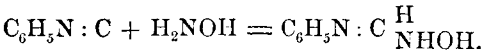
0.1549 gram substance, dried over H_2SO_4 in a vacuum, gave 0.3452 gram CO_2 and 0.0848 gram H_2O.

0.1526 gram substance, dried over H_2SO_4 in a vacuum, gave 0.3428 gram CO_2 and 0.0843 gram H_2O.

0.1544 gram substance gave 28.5 c.cm. N_2 at 20° and 755 mm.

	Theory for $C_7H_8N_2O$.	Found		
C	61.76	60.87	60.78	61.27
H	5.89	6.18	6.08	6.14
N	20.59	20.97		

In order to prove absolutely that the substance was really phenylisuretine it was necessary to obtain it synthetically from a formic acid derivative. To effect this, two ways were open; the substance could, in the first place, easily be formed from phenylisocyanide and hydroxylamine, by addition,



$$C_6H_5N : C + H_2NOH = C_6H_5N : C \begin{matrix} H \\ NHOH \end{matrix}.$$

In the second place, it could probably easily be obtained from isuretine by means of aniline hydrochloride.

The second method was first chosen, and since this succeeded directly and quantitatively, the first way, which in all probability would also yield phenylisuretine, was not tried.

Preparation of Isuretine, $HN : C \begin{matrix} H \\ NHOH \end{matrix}$. — Lossen and Schifferdecker have obtained this compound from prussic acid and hydroxylamine.† The following slight modification of their method gives a very good yield of isuretine. A solution of 30 grams of cyanide of potash in 60 grams of water, is added to a solution of 31.5 grams hydroxylaminehydrochloride (one molecule) in 60 c.cm. water; great care must be taken that the temperature never rises above 5°. The solution is kept for 48 hours at 5°, and then allowed to evaporate spontaneously in flat dishes. The dry residue is boiled out with absolute alcohol, and on cooling and evaporating the filtrates, isuretine separates out in colorless needles, melting at 114°–115°. The last portions separating out are best crystallized from acetic ether, from which the substance is obtained perfectly pure and beautifully crystalized. With the exception of the melting point (Lossen and Schifferdecker give mpt. 104°–105°), the former statements concerning its properties could be confirmed.

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* Ann. Chem. (Liebig), CCLXX. 276.

† Ibid., CLXVI 295.

The yield is 84 grams pure isuretine from 142 grams cyanide of potash used.

0.2531 gram substance, dried over H_2SO_4 in a vacuum, gave 0.1872 gram CO_2 and 0.1571 gram H_2O.

0.1369 gram substance, dried over H_2SO_4 in a vacuum, gave 56.7 c.cm. N_2 at 21° and 753 mm.

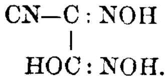
	Theory for CN_2H_4O.	Found.
C	20.00	20.17
H	6.67	6.89
N	46.67	46.71

Phenylisuretine from Isuretine. — On heating isuretine (1 gram) and aniline hydrochloride (one molecule) in alcoholic solution, an interaction with formation of phenylisuretine and ammonium chloride very soon takes place. After distilling off the alcohol, and treating the residue with cold water to get rid of ammonium chloride, it is crystallized from ether; 1.7 grams of phenylisuretine were obtained, crystallizing in flat needles, melting at 138°, and in every respect identical with the compound obtained from formylchloridoxime.

0.0687 gram substance, dried over H_2SO_4 in a vacuum, gave 13 c.cm. N_2 at 24° and 755 mm.

	Theory for $C_7H_8N_2O$.	Found.
N	20.59	21.07

Behavior of Formylchloridoxime towards Ammonia.

Cyanisonitrosoacethydroxamic Acid, 

$$\begin{array}{l} CN{-}C:NOH \\ \quad | \\ HOC:NOH. \end{array}$$

— In view of the results with aniline, it was at first expected that, on treating formylchloridoxime with ammonia, isuretine and ammonium chloride would be formed. The reaction takes place, however, in a different manner, no matter whether the ethereal solution of formylchloridoxime is treated with concentrated aqueous, or with dry gaseous ammonia. It is best to proceed as follows. The ethereal solution, obtained by extracting the acidified sodium fulminate solution, is treated directly, without concentrating it, in a separatory funnel with small quantities of concentrated aqueous ammonia (30 per cent), taking care to shake well and to cool thoroughly with water. A yellow powder separates out in large quantity, which settles on shaking in the lower portion of the funnel. A portion from 32 grams of mercuric fulminate was always worked up at a time, and about 40–50 c.cm. concentrated ammonia used (until a strong smell of ammonia is apparent). The aqueous solution with the yellow powder suspended in it, is then drawn off and filtered, and the filtrate again brought into the separatory funnel, and the operation repeated until all the yellow powder is brought on the filter; it is then dried on clay plates. The filtrate contains much ammonium chloride and also some of the yellow substance, which is sparingly soluble in cold water. 25 grams of the yellow powder were regularly obtained from 96 grams of mercury fulminate: it consists of the secondary ammonium salt of cyanisonitrosoacethydroxamic acid; it cannot be crystallized from hot water however without some decomposition. The yellow powder is therefore converted directly into the free acid. 25 grams of the salt are suspended in 40 c.cm. water, and 120 c.cm. dilute hydrochloric acid (16.5 per cent) added, and thereupon the resulting solution is extracted 35 times with ether. After drying with chloride of calcium, the ethereal solution is distilled off and 15 grams of a colorless solid remains, which already consists of practically pure cyanisonitrosoacethydroxamic acid. The substance is recrystallized from ether with addition of a small amount of ligroine (bpt. 70°–80°), and obtained in colorless cubes or in 4-sided prisms, clear as glass, and melting, with decomposition, at 117°–118°.

0.1555 gram substance, dried over H_2SO_4 in a vacuum, gave 0.1490 gram CO_2 and 0.0438 gram H_2O.

0.1125 gram substance, gave 30.5 c.cm. N_2 at 20° and 751 mm.

	Theory for $C_3H_3N_3O_3 . \frac{1}{2} H_2O$.	Found.
C	26.09	26.13
H	2.90	3.13
N	30.43	30.64

The substance is readily soluble in water, and in organic solvents with the exception of benzene and ligroine. It crystallizes from acetic acid in transparent quadratic pyramids with basal planes. The substance has a strong acid smell, and gives both primary and secondary salts, which are colored yellow. An aqueous solution of the acid gives with ferric chloride an intense blood-red coloration.

Primary Silver Salt, $C_3H_2N_3O_3Ag$. — This salt separates out slowly in yellow flat prisms on addition of silver nitrate (one molecule) to a concentrated aqueous solution of the acid. The filtrate gives, on long standing, a brownish red precipitate.

0.1948 gram substance, dried over H_2SO_4 in a vacuum, gave 0.1172 gram AgCl.

	Theory for $C_3H_2N_3O_3Ag$.	Found.
Ag	45.76	45.29

Secondary Potassium Salt, $C_3HN_3O_3K_2$, H_2O. — This salt is obtained quantitatively on adding an alcoholic solution of the acid to an alcoholic solution of potassic hydrate (two molecules). It separates out as a yellow crystalline powder, which, after being well washed with alcohol and dried over sulphuric acid in a vacuum, was analyzed.

0.2038 gram substance gave 0.1596 gram K_2SO_4.

	Theory for $C_3HN_3O_3K_2H_2O$.	Found.
K	34.98	35.11

Behavior of the Acid towards Ammonia. — On adding concentrated ammonia solution to an aqueous solution of cyanisonitrosoacethydroxamic acid, the secondary ammonium salt separates out as a yellow amorphous powder, identical with the salt obtained directly from formylchloridoxime and ammonia. If, however, much ammonia solution is used, a yellow solution results, in which, after some standing, no longer the original substance, but its decomposition products are present. These are the products which Ehrenberg (see above) obtained on treating his ethereal formylchloridoxime solution with a large quantity of aqueous ammonia. The primary product of the reaction, the ammonium salt of cyanisonitrosoacethydroxamic acid, was obtained by him only in traces, and was not further investigated.* It simply remained dissolved in the aqueous ammonia solution, because he used a very large amount of the solution. He obtained, on allowing this solution to stand in the air, three compounds. First, a substance,† $C_3H_4N_4O_2$, which separates out in yellow needles; on acidifying and extracting with ether, two other compounds were obtained: one of these, which is far less soluble in cold ether, he calls isofulminuric acid,* and its composition as $C_3H_3N_3O_3$ was determined by many analyses; the other substance was a syrupy acid from which he obtained a small amount of a crystallized ammonium salt, $C_3H_7N_5O_3$.†

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* Journ. f. prakt. Chem., [2.], XXX. 47.

† Ibid., XXX. 49.

These three substances are all obtained by allowing an ammoniacal solution of pure cyanisonitroacethydroxamic acid to stand in the air, and proceeding according to the directions of Ehrenberg. It is to be noted that Ehrenberg's compound of the formula $C_3H_4N_4O_2$ possesses weak acid as well as also strong basic properties; it dissolves therefore instantly in cold dilute hydrogen chloride. It also gives with ferric chloride an intense blood-red coloration.

Behavior of Cyanisonitrosoacethydroxamic Acid towards Water. — Whereas a solution of the free acid in concentrated hydrochloric acid or in concentrated sulphuric acid can be kept without essential change for twelve hours in the cold, an aqueous solution of the acid (2 grams) is completely decomposed after two hours heating on a water bath. The solution no longer gives a yellow but a white precipitate with silver nitrate. On extracting with ether, and drying the ethereal solution with calcic chloride, two substances are obtained which are identical with Ehrenberg's isofulminuric acid and his syrupy acid. The former can easily be separated from the latter by washing with a small amount of ether. It was crystallized (1 gram) from a small amount of water, and obtained as a white spongy powder identical in its properties and its behavior with Ehrenberg's isofulminuric acid. The fact that the substance gives with ferric chloride a deep blood-red coloration is worthy of mention.

0.1687 gram substance, dried at 100°, gave 0.1725 gram CO_2 and 0.0386 gram H_2O.

0.0780 gram substance, dried at 100°, gave 23 c.cm. N_2 at 22° and 750 mm.

	Theory for $C_3H_3N_3O_3$.	Found.
C	27.91	27.89
H	2.33	2.54
N	32.56	32.94

The syrupy acid which is formed at the same time is identical with the corresponding compound obtained by Ehrenberg, but for the present has not been further studied.

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* Journ. f. prakt. Chem., [2.], XXX. 55.

† Ibid., XXX. 59.

Behavior of the Acid $C_3H_3N_3O_3, \frac{1}{2} H_2O$, *towards concentrated Caustic Potash.* — In the expectation that cyanisonitrosoacethydroxamic acid must, by treatment with caustic potash, yield potassic isonitrosomalonate, it was heated (1 gram) with concentrated potassic hydrate (6.9 grams KOH and 10 grams water) for three quarters of an hour on a water bath. Ammonia is given off copiously, and the solution is then treated further according to the method of Baeyer.* On addition of alcohol to the solution, acidulated with acetic acid, an oily precipitate is obtained, which, on rubbing with a glass rod, solidifies. Recrystallized once from water and alcohol, it is obtained (0.5 gram) in colorless leaflets, which give with ferric chloride a deep red coloration, and which resemble very closely potassic isonitrosomalonate. The analysis of the salt, dried over sulphuric acid in a vacuum, showed, however, that another substance is at hand, and that the original acid has lost *only one atom of nitrogen* as ammonia in the above treatment.

0.2498 gram substance gave 32.5 c.cm. N_2 at 20° and 746 mm.
0.2024 gram substance gave 0.0988 gram K_2SO_4.

	Theory for $C_3HN_2O_4K,H_2O$.	Found.
N	15.04	14.61
K	21.04	21.89

Behavior of the Acid $C_3H_3N_3O_3, \frac{1}{2} H_2O$, *towards concentrated Hydrogen Chloride.* — 2 grams of the acid are heated in a sealed tube for five hours with concentrated hydrochloric acid (10 c.cm. of sp. gr. 1.18). On opening the tube, the presence of carbon dioxide was noticed; and on evaporating the contents on a water bath, 2.5 grams of residue are regularly obtained. On digesting this with ether, the oxalic acid formed in the reaction (proved by its tests and properties) was removed, and the residue (2 grams) consists of a mixture of much ammonic chloride and of little hydroxylamine hydrochloride. A quantitative determination, carried out by means of Fehling's solution, showed that the residue (2 grams) consists of 1.6 grams ammonium chloride and of 0.4 grams hydroxylamine hydrochloride.

It follows from these experiments that cyanisonitrosoacethydroxamic acid is decomposed by hydrogen chloride into oxalic acid, carbon dioxide, ammonium chloride, and oxyammonium chloride; and that more than two thirds of its nitrogen is eliminated in the form of ammonic chloride.

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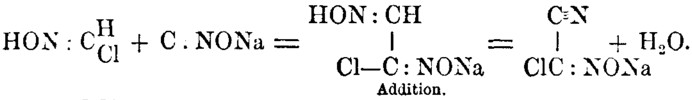
* Ann. Chem. (Liebig), CXXXI. 292.

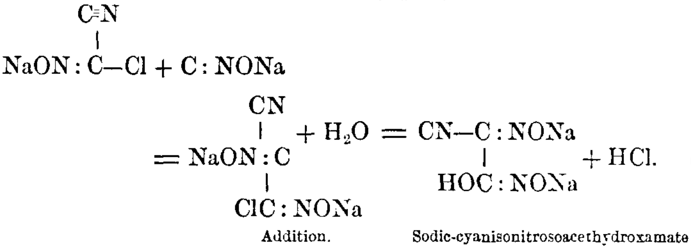
The Constitution of the Acid. — That the acid, $C_3H_3N_3O_3, \frac{1}{2} H_2O$, obtained from formylchloridoxime by means of ammonia, is identical with cyanisonitrosoacethydroxamic acid cannot at present be determined with certainty from its decomposition products. The constitution of the acid as given is however extremely probable *because of its quantitative formation* from sodic fulminate (two molecules) and formylchloridoxime.

The action of formylchloridoxime on sodic fulminate can, because of the entirely analogous results obtained with phosgene on isocyanides,* take place only in the following manner.



$$HON{:}C\begin{smallmatrix}H\\Cl\end{smallmatrix} + C{:}NONa = \begin{array}{c}HON{:}CH\\|\\Cl{-}C{:}NONa\end{array} = \begin{array}{c}C\equiv N\\|\\ClC{:}NONa\end{array} + H_2O. \quad (I.)$$

Addition.

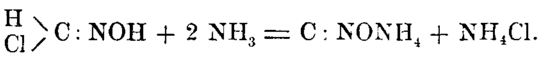


$$\begin{array}{l}C\equiv N\\|\\NaON{:}C{-}Cl\end{array} + C{:}NONa$$

$$= NaON{:}\begin{array}{c}CN\\|\\C\\|\\ClC{:}NONa\end{array} + H_2O = \begin{array}{c}CN{-}C{:}NONa\\|\\HOC{:}NONa\end{array} + HCl. \quad (II.)$$

Addition. Sodic-cyanisonitrosoacethydroxamate.

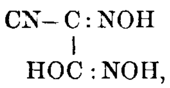
The reaction which takes place on treating formylchloridoxime with ammonia is entirely analogous: a decomposition of the formylchloridoxime into ammonium chloride and ammonic fulminate first takes place as follows:



$$\begin{smallmatrix}H\\Cl\end{smallmatrix}\!>C{:}NOH + 2\,NH_3 = C{:}NONH_4 + NH_4Cl.$$

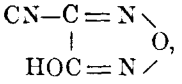
The ammonic fulminate thus formed (two molecules) then reacts with unchanged formylchloridoxime (just as in the above equations does sodic fulminate) and ammonic cyanisonitrosoacethydroxamate is formed.

As can easily be seen, cyanisonitrosoacethydroxamic acid,



$$\begin{array}{c}CN{-}C{:}NOH\\|\\HOC{:}NOH,\end{array}$$

can readily go over by loss of water into a furazane derivative,



$$\begin{array}{c}CN{-}C{=}N\diagdown\\|\qquad O,\\HOC{=}N\diagup\end{array}$$

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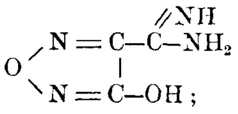
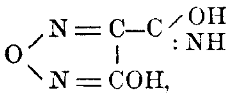
* Ann. Chem. (Liebig), CCLXX. 286, 315.

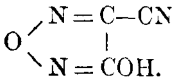
and this suffices to explain fully all the reactions and decomposition products of this acid. That the furazane ring is a very stable one is clearly evident from the experiments of Wolff.* Ehrenberg's product, $C_3H_4N_4O_2$, is therefore very probably



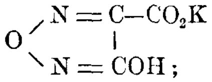
his isofulminuric acid is identical with oxyfurazane-carbonicamide,



whereas the syrupy acid obtained by him is probably oxyfurazane-cyanide,

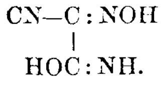


The product obtained by myself, by means of concentrated potassic hydrate, $C_3HN_2O_4K$, H_2O, is, on the other hand, probably identical with potassic oxyfurazanecarboxylate,



it must therefore be obtained from all three of Ehrenberg's compounds by saponification. Further experiments, with a view of proving more sharply the constitution of these decomposition products of cyanisonitrosoacethydroxamic acid, will be taken up again shortly.

III. DESOXYFULMINURIC ACID IS IDENTICAL WITH CYANISONITROSOACETAMIDE,



$$\begin{array}{l} CN{-}C:NOH \\ \quad | \\ HOC:NH. \end{array}$$

Liebig† and Schischkoff‡ have shown that on boiling mercuric fulminate with ammonic chloride, or with potassic chloride and water, a monobasic acid, $HC_3H_2N_3O_3$, is formed which, at present, is known by the name of fulminuric acid. Ehrenberg § obtained the same acid

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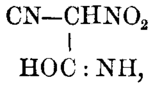
[*] Ann. Chem. (Liebig), CCLX. 101. Cf. Ber. d. chem. Ges., XXIV. 1167.

[†] Ann. Chem. (Liebig), XCV. 282.

[‡] Ibid., XCVII. 53, CI. 213.

[§] Journ. f. prakt. Chem., [2.], XXXII. 98.

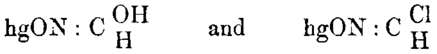
by boiling fulminate of mercury with water. Among the many formulæ which have been advanced as representing the constitution of this acid, the one proposed by Steiner,*



$$\begin{array}{c}CN{-}CHNO_2\\ |\\ HOC:NH,\end{array}$$

possesses the greatest probability. It explains very simply the formation of nitroacetonitrile, $CN{-}CH_2NO_2$, from it by means of sulphuric acid,† as well as the formation of trinitroacetonitrile, $CN{-}C(NO_2)_3$, by means of sulphuric acid and nitric acid. ‡

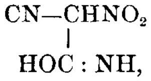
It follows directly from the above experiments, that, on boiling mercuric fulminate with water and either ammonic chloride or potassic chloride, an addition of water or of hydrogen chloride to the unsaturated carbon atom present in this salt must at first take place, and thus the products



$$hgON:C\begin{array}{l}OH\\ H\end{array} \quad \text{and} \quad hgON:C\begin{array}{l}Cl\\ H\end{array}$$

must be formed. These can then act further, in the second stage, on unchanged mercuric fulminate in exactly the same way as formylchloridoxime acts on sodic fulminate (see above). It was therefore suspected for a long time that cyanisonitrosoacethydroxamic acid must be an intermediate product in the formation of fulminuric acid (its isomer). After, however, many fruitless attempts were made to convert this substance into fulminuric acid, by oxidation, by boiling with mercuric oxide, or with ammonia and oxide of mercury, etc., it seems to me impossible that this is formed as an intermediate product.

If fulminic acid is identical with nitrocyanacetamide,



$$\begin{array}{c}CN{-}CHNO_2\\ |\\ HOC:NH,\end{array}$$

and this is proved to be the case farther on, it must be formed from mercury fulminate in a manner entirely analogous, for instance, to the formation of mesoxanilide from phenylisocyanide, phosgene, and water,§ or also to that of cyanisonitrosoacethydroxamic acid from formylchloridoxime and soluble fulminic acid salts. The following explanation of the reaction which takes place in the formation of fulminuric acid seems to me at present to be the most plausible one. The product first formed by the action of ammonic chloride on mercury fulminate,*

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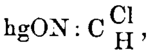
* Ber. d. chem. Ges., IX. 784.

† Steiner, Ber. d. chem. Ges., IX. 782.

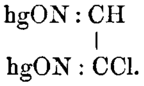
‡ Schischkoff, Ann. de Chim. et de Phys., [3.], XLIX. 310.

§ Ann. Chem. (Liebig), CCLXX. 291.



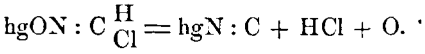
$$\mathrm{hgON : C}\begin{smallmatrix}\mathrm{Cl} \\ \mathrm{H}\end{smallmatrix},$$

reacts first on the unchanged salt, giving by addition



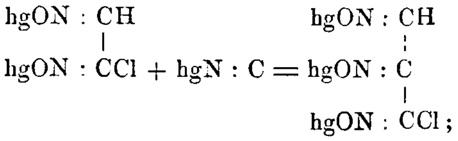
$$\begin{array}{l}\mathrm{hgON : CH} \\ \qquad\quad | \\ \mathrm{hgON : CCl.}\end{array} \qquad \text{(I.)}$$

Mercury formylchlorid-oxime is, however, as is readily understood and has also been proved,† a strong oxidizing agent, which can easily go over, with loss of oxygen, into cyanide of mercury,



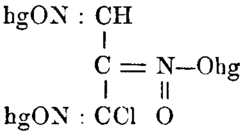
$$\mathrm{hgON : C}\begin{smallmatrix}\mathrm{H} \\ \mathrm{Cl}\end{smallmatrix} = \mathrm{hgN : C + HCl + O.}$$

The cyanide of mercury thus formed, can then react with the addition product (I.) as follows :



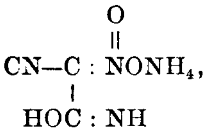
$$\begin{array}{lcl}\mathrm{hgON : CH} & & \mathrm{hgON : CH} \\ \qquad\quad | & & \qquad\quad \vdots \\ \mathrm{hgON : CCl + hgN : C} & = & \mathrm{hgON : C} \\ & & \qquad\quad | \\ & & \mathrm{hgON : CCl\,;}\end{array} \qquad \text{(II.)}$$

and this product is then oxidized to



$$\begin{array}{l}\mathrm{hgON : CH} \\ \qquad\quad | \\ \qquad\quad \mathrm{C = N{-}Ohg} \\ \qquad\quad |\quad\;\; \| \\ \mathrm{hgON : CCl\;\; O}\end{array} \qquad \text{(III.)}$$

from which, by means of ammonia, the ammonium salt of fulminuric acid,



$$\begin{array}{l}\qquad\quad \mathrm{O} \\ \qquad\quad \| \\ \mathrm{CN{-}C : NONH_4,} \\ \quad\;\; | \\ \mathrm{HOC : NH}\end{array}$$

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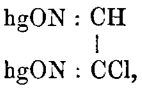
* The reaction with water is entirely analogous; it is only necessary to substitute OH for Cl.

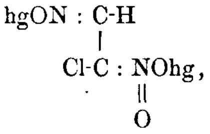
† An aqueous solution of formylchloridoxime oxidizes, for example, ferrous salts in acid solution immediately in the cold, and prussic acid is set free. Cf. also Schischkoff, Ann. Chem. (Liebig), Suppl. Vol., I. 108.

can readily be formed. It is, however, also possible that the addition product I.,



$$\begin{array}{c}\mathrm{hgON : CH}\\ |\\ \mathrm{hgON : CCl},\end{array}$$

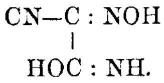
first goes over, by oxidation, into



$$\begin{array}{l}\mathrm{hgON : C\text{-}H}\\ \qquad\quad |\\ \qquad\mathrm{Cl\text{-}C : NOhg},\\ \qquad\qquad\ \ \|\\ \qquad\qquad\ \ \mathrm{O}\end{array}$$

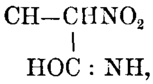
which then can add itself to cyanide of mercury, C : Nhg, present, giving directly the addition product III., which, with ammonia, gives mercuric oxide and ammonic fulminurate.

Synthesis of Cyanisonitrosoacetamide,



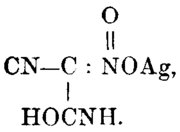
$$\begin{array}{c}\mathrm{CN{-}C : NOH}\\ |\\ \mathrm{HOC : NH}.\end{array}$$

Seidel[*] has recently obtained, on treating silver fulminurate with ethyliodide, a substance, $C_3H_2N_3O_3(C_2H_5)$, which, on boiling with water, decomposes into acetaldehyde, C_2H_4O, and a substance having the formula $C_3H_3N_3O_2$, which he therefore calls desoxyfulminuric acid. If fulminuric acid is identical with nitrocyanacetamide,



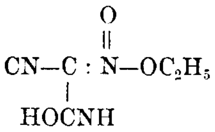
$$\begin{array}{c}\mathrm{CH{-}CHNO_2}\\ |\\ \mathrm{HOC : NH},\end{array}$$

it follows, by reason of the experiments on nitro compounds presented in the preceding paper, that, on treating the silver salt of fulminuric acid,



$$\begin{array}{l}\qquad\quad\ \mathrm{O}\\ \qquad\quad\ \|\\ \mathrm{CN{-}C : NOAg},\\ \qquad |\\ \ \mathrm{HOCNH}.\end{array}$$

with ethyliodide, an ester of the constitution



$$\begin{array}{l}\qquad\quad\ \mathrm{O}\\ \qquad\quad\ \|\\ \mathrm{CN{-}C : N{-}OC_2H_5}\\ \qquad |\\ \ \mathrm{HOCNH}\end{array}$$

must be formed.

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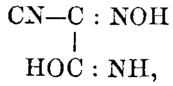
[*] Ber d. chem. Ges., XXV. 431 and 2756.

This ester must then, on boiling with water, be split by intra-molecular oxidation into cyanisonitrosoacetamide,



$$\begin{array}{c} CN{-}C : NOH \\ | \\ HOC : NH, \end{array}$$

and into acetaldehyde, $CH_3CH : O$. These considerations lead to the conclusion that desoxyfulminuric acid must be identical with cyanisonitrosoacetamide, and the following experiments, which have led to a synthesis of this compound, prove that in fact both products are absolutely identical.

Cyanisonitrosoacetic ether, as well as cyanisonitrosoacetic acid, have recently been obtained by Muller* from cyanacetic ether. I also have made both these compounds in this way, and can confirm the statements of Muller completely, except that the melting point of cyanisonitrosoacetic ethylester was found to be 133° instead of 128°–129°, when the substance is crystallized from benzene. Both compounds were analyzed, and gave figures agreeing well with the theoretical ones. It is somewhat noteworthy that the ester melts higher than the free cyanisonitrosoacetic acid.

On heating cyanisonitrosoacetic ethylester (2 grams) in a sealed tube with 10 c.cm. of alcoholic ammonia for four hours at 100°, a salt separates out, on cooling, in yellow heavy nodules. It is filtered off, well washed with alcohol, dissolved in hydrochloric acid, and extracted with ether. After drying the ethereal solution with calcic chloride, and concentrating, colorless heavy plates separate out, which, recrystallized once more from ether, melt at 184° and are perfectly pure.

0.1997 gram substance, dried over H_2SO_4 in a vacuum, gave 0.2325 gram CO_2 and 0.0520 gram H_2O.

0.1515 gram substance, gave 50.2 c.cm. N_2 at 19° and 744 mm.

	Theory for $C_3H_3N_3O_2$.	Found.
C	31.86	31.75
H	2.66	2.89
N	37.17	37.27

The substance crystallizes either in needles, or in heavy many-sided flat crystals, and is identical in every respect with Seidel's desoxyfulminuric acid. In order to be absolutely certain, this substance was made according to Seidel's directions, and compared in every detail with the synthetic product; no difference could be detected between them. Furthermore, desoxyfulminuric acid made from mercury fulminate is converted quantitatively into cyanisonitrosoacetic acid and into isonitrosomalonic acid, as is evident from the following experiments.

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* Annales de Chim. et de Phys., [7.], I. 504.

3 grams desoxyfulminuric acid were heated on a water bath for one hour with 2.2 grams sodic hydrate and 40 c.cm. water, whereby a copious evolution of ammonia was noticed; the solution was acidified with dilute sulphuric acid, and extracted with ether. After evaporating the ether, the residual oil (1.6 grams) slowly solidifies. It was twice crystallized from a mixture of ether and benzene, and obtained in colorless needles, melting at 103°. The substance was identical with cyanisonitrosoacetic acid prepared from cyanacetic ether.*

0.2048 gram substance, dried over H_2SO_4 in a vacuum, gave 0.2190 gram CO_2 and 0.0495 gram H_2O.
0.1251 gram substance gave 25.2 c.cm. N_2 at 19° and 752 mm.

	Theory for $C_3H_2N_2O_3, \frac{1}{2}H_2O$.	Found.
C	29.27	29.16
H	2.44	2.68
N	22.76	22.97

It is noteworthy that cyanisonitrosoacetic acid, which has now been obtained in four different ways,† always contains half a molecule of crystal water.

0.8 gram desoxyfulminuric acid, 2.5 grams caustic potash, and 5 c.cm. water, were heated for 3 hours on a water bath, and then worked up according to the method of Baeyer ‡ for potassic isonitrosomalonate. The salt was recrystallized twice, and 0.95 gram was obtained. The analysis agrees with theory for anhydrous salt.

0.2250 gram substance, dried over H_2SO_4 in a vacuum, gave 0.1844 gram K_2SO_4.
0.2520 gram substance gave 16 c.cm. N_2 at 24° and 744 mm.
0.3030 gram substance gave 0.1906 gram CO_2 and 0.0175 gram H_2O.

	Theory for $C_3HO_5K_2N$	Found.
C	17.22	17.15
H	0.48	0.64
N	6.70	6.96
K	37.32	36.74

---

* Annales de Chim. et de Phys., [7.], I. 504.

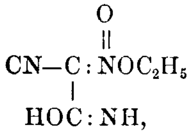
† Ann. Chem. (Liebig), CXXXI. 295.

‡ Wolff and Gans, Ber. d. chem. Ges., XXIV. 1169; Söderbaum, Ber. d. chem. Ges., XXIV. 1231 and 1989; Muller, Annales de Chim. et de Phys., [7.], I. 504.

Seidel obtained by heating silver fulminurate[*] with ethyliodide at 100°, instead of at 80°, a second compound of the formula,

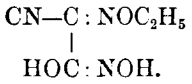
$$C_3H_2N_3O_3(C_2H_5),$$

melting point 155°.[†] This is in all probability formed from the normal and original ester,



$$\begin{array}{l} \quad\quad\; O \\ \quad\quad\; \| \\ CN-C:NOC_2H_5 \\ \quad\;\; | \\ \;\; HOC:NH, \end{array}$$

by a molecular rearrangement, especially since we now know that such esters are unstable compounds, capable of intramolecular oxidation. It is very probable that this second compound, $C_3H_2N_3O_3(C_2H_5)$, possesses the constitution



$$\begin{array}{l} CN-C:NOC_2H_5 \\ \quad\;\; | \\ \;\; HOC:NOH. \end{array}$$

It is a strong acid, — a fact which Seidel does not mention.

IV. Sodicferrofulminate, $Na_4Fe(ON:C)_6 + 18 H_2O$.

The remarkable resemblance of fulminic acid, C:NOH, and its salts, C:NOM, to prussic acid, C:NH, and its salts, C:NM, has become very evident by reason of the facts presented above. This resemblance is so great, that many observers have been led astray in working with fulminic acid compounds. For this reason it seems to me that *no longer the slightest doubt can exist* concerning the nature of prussic acid and its salts.[‡] *They are unquestionably all derivatives of isocyanogen.*

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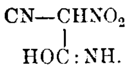
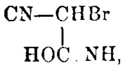
[*] It need hardly be mentioned that many fruitless experiments were carried out in the hope of synthesizing fulminuric acid, which, according to the above results, must be identical with nitrocyanacetamide,



$$\begin{array}{l} CN-CHNO_2 \\ \quad\;\; | \\ \;\; HOC:NH. \end{array}$$

Bromcyanacetamide,

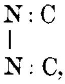


$$\begin{array}{l} CN-CHBr \\ \quad\;\; | \\ \;\; HOC:NH, \end{array}$$

mpt. 122°, can easily be made from cyanacetamide, bromine, and water, but all attempts to convert it, by means of potassic or silver nitrite, into nitrocyanacetamide were attended with negative results.

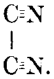
[†] Ber. d. chem. Ges., XXV. 2756.

[‡] Ann. Chem. (Liebig), CCLXX. 329.



$$\begin{array}{l} N:C \\ | \\ N:C, \end{array}$$

and not, as has so long been supposed, derivatives of cyanogen,



$$\begin{array}{l} C\equiv N \\ | \\ C\equiv N. \end{array}$$

The analogy between fulminic acid and prussic acid is further shown by the isolation of a double salt, sodic ferrofulminate,

$$Na_4Fe(ON.C)_6$$

corresponding completely with sodic ferrocyanide,

$$Na_4Fe(N:C)_6.$$

Carstanjen and Ehrenberg have already drawn attention to the very peculiar behavior of sodic fulminate towards iron salts, and shown that solutions result in which the presence of iron can no longer be detected.*

On adding to an aqueous solution of sodic fulminate containing some sodic hydrate, and obtained as stated above from mercuric fulminate (32 grams), a solution of ferrous sulphate (one molecule to six molecules sodic fulminate), a yellowish solution is obtained, in which the presence of iron cannot be detected either by means of sodic hydrate or of ammonium sulphide. The filtered solution is allowed to evaporate spontaneously in flat dishes in the air, and after some time beautiful yellow needles, often over an inch in length, separate out. It is easily possible to obtain 11 grams of this substance in a perfectly pure state from the above amount of mercury fulminate taken. The crystals are filtered off, washed with a small amount of cold water, and then dried between filter paper; they do not contain a trace of sodium sulphate.

On further evaporation of the mother liquors, more of the salt separates out, but mixed with Glauber's salt. The sodic ferrofulminate thus obtained is freely soluble in cold water, and gives with ferric chloride an intense purple-red coloration, which is incredibly delicate. The pure substance is, however, unstable in aqueous solutions or in a moist condition, and soon gets colored purplish red; the presence of sodic hydrate increases its stability, and for this reason it is well to recrystallize in the presence of a small amount of sodic hydrate. The salt contains 18 molecules of crystal water, a portion of which goes off quickly in the air or over sulphuric acid in a vacuum, and the substance changes its color first to white and then slowly to red. A concentrated aqueous solution of the salt is precipitated by alcohol. first in yellow needles, and on addition of more alcohol these are suddenly transformed into a colorless white powder with loss of a portion of the crystal water.

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* Journ. f. prakt. Chem., [2.], XXV. 246, 247.

Whereas, the double salt, $AgON:C, KON:C$, is far more stable than the corresponding prussic acid double salt, $AgN:C, KN:C$, in this case the ferrofulminate of soda is far less stable than the analogous sodic-ferrocyanide. It does not give an acid, ferrofulminic acid corresponding to ferrocyanic acid, and, even on losing its crystal water, the salt $Na_6Fe(ON:C)_6 + 18\,H_2O$ dissociates completely into sodic fulminate, $NaON:C$, and into ferrous fulminate, $Fe(ON:C)_2$.

On treating the salt in the cold with dilute hydrochloric acid, it is converted into formylchloridoxime. Also on boiling it in aqueous solution with sodic hydrate or with ammonium sulphide, it is slowly decomposed, with separation of iron hydrate or iron sulphide.

An aqueous solution of the salt gives with lead acetate, silver nitrate, or mercuric chloride, white very explosive precipitates, which appear to consist exclusively of the corresponding fulminic acid salts.

As mentioned above, the yellow salt easily loses a portion of its crystal water and becomes colored white; on addition of water, it is again transformed completely into the original salt. After long standing over sulphuric acid in a vacuum, the white salt becomes tinged red, and finally is converted into a red powder, which no longer consists of ferrofulminate of soda, but of a mixture of sodic fulminate and ferrous fulminate; it then dissolves only partly in water, leaving behind a red powder, and the solution does not contain a trace of sodic ferrofulminate. On adding sodic hydrate, however, union of the components again takes place, and the solution contains sodic ferrofulminate, which can be obtained on allowing the solution to evaporate.

The red dissociated salt just mentioned possesses very explosive properties. It is just as dangerous as sodic fulminate,* and on this account it was never possible to carry out a complete analysis of the salt; even when mixed very carefully with oxide of copper, on heating invariably a violent explosion took place.† The quantitative determination of the iron and sodium offered at first some difficulty, because, on decomposing the salt with hydrochloric and nitric acids, always a small amount of substance crystallizing in green leaflets is formed, which is insoluble in aqua regia. The salt was finally decomposed by treating first with a small amount of dilute sulphuric acid, and then evaporating to dryness and igniting. The residue was then dissolved in hydrochloric acid, with addition of a small amount of nitric acid, and the iron and sodium determined in the usual way.

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* Journ. f. prakt. Chem., [2.], XXXII. 231.

† The explosion is so sudden that not a gas bubble appears in the potash bulb (5 times noticed), and the combustion tube is shattered completely only where the substance was present.

4.754 grams yellow salt, dried between filter paper, lost on standing over H_2SO_4 in a vacuum, after two days, 1.5806 grams H_2O: after four days, 1.8167 grams H_2O; after six days, 1.8996 grams H_2O; on further standing, no further loss of weight was noticed.

	Theory for $Na_4Fe(ONC)_6\,2\,H_2O + 16\,H_2O$.	Found.
16 H_2O	39.80	39.96

The red powder remaining is very hygroscopic, and still contains two molecules of crystal water.

1.0073 grams substance gave 0.1760 gram Fe_2O_3.
0.8154 gram substance gave 0.5380 gram Na_2SO_4.
0.6999 gram substance gave 0.1282 gram Fe_2O_3 and 0.4609 gram Na_2SO_4.

	Theory for $Na_4Fe(ONC)_6\,2\,H_2O$	Found.	
Na	21.10	21.36	21.33
Fe	12.84	12.12	12.73

An attempt was made to obtain, by oxidation of this salt with bromine and water, a fulminic acid double salt corresponding to sodic ferricyanide, but without success.

V. ON FULMINIC ACID AND ITS ESTERS. — THE CARBYLOXIMESTERS, C : NOR.

The experiments described above make it clear that it is not possible to obtain free fulminic acid from its salts by treatment with acids, because the acids always react first on the tremendously reactive bivalent carbon atom present in these salts; and for this reason oximes of formic acid derivatives are invariably obtained, which, although they can readily be converted back again into fulminic acid salts, never yield, when they decompose, the free fulminic acid. In this connection an experiment carried out with isuretine is of interest. On heating alcoholic solutions of isuretine and hydroxylamine hydrochloride (in molecular quantities) an interaction with formation of ammonium chloride and of oxyisuretine very quickly takes place. On attempting to distil off the alcohol, white fumes are noticed, which decompose with some violence and the solution has an odor resembling very closely that of prussic acid. On evaporating the solution over sulphuric acid in a vacuum, a yellow coloration is noticed (after most of the alcohol has disappeared), and after a short time the residue decomposes spontaneously with a hissing noise and tremendous evolution of heat. It follows from this experiment that oxyisuretine,

$$HON : C^{H}_{NHOH},$$

is a very unstable substance, and decomposes probably at first into carbyloxime, $C : NOH$, and into hydroxylamine. This decomposition is entirely analogous to that of phenylisuretine,

$$C_6H_5N : C^{H}_{NHOH},$$

and also especially to that of formylsulphate-oxime,

$$HON : C^{H}_{OSO_2OH},$$

and of formylchloridoxime,

$$HON : C^{H}_{Cl}.$$

The sum total of the results presented in this paper lead to the conclusion that the free fulminic acid is a very unstable compound, which possesses a smell that cannot be distinguished from that of prussic acid. It follows further, however, that a series of ethers of this acid must exist of the general formula $C : NOR$, which must in their properties and their odor show the greatest resemblance to the esters of prussic acid, the alkylisocyanides, $RN : C$. Although I have not yet succeeded in isolating and analyzing a carbyloximether, $C : NOR$, the following observations are sufficient to make it extremely probable that such esters do exist.

The Action of Ethyliodide on Silver Fulminate.— Calmels * states, that on treating silver fulminate with ethyliodide, α and β nitropropylene and ethylisocyanide are formed. I have repeated his experiments, and observed that, on heating silver fulminate with ethyliodide and absolute ether to 50°, or on allowing these substances to stand at ordinary temperature, after a time most tremendous explosions take place ; these can be entirely avoided as follows. 28.7 grams silver fulminate, 50 grams ethyliodide, and 38 grams absolute ether are brought into a flask, which is constantly kept in cold water, and allowed to stand thus for three weeks, taking care to shake well from time to time. At first, in the course of the reaction, a very strong smell of ethylcyanate is noticed (Calmels says smell of chlorpicrin) and towards the end a smell resembling that of ethylisocyanide is noticed.

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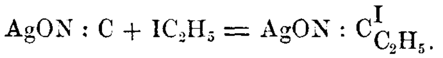
* Comptes Rendus, XCIX. 794

The investigation of the products formed has shown that they *consist chiefly of ethylcyanate and its polymer ethylcyanurate*, whereas very little of the substance smelling like ethylisocyanide is formed. It seems to me, however, extremely probable that this product is not ethylisocyanide, but ethylcarbyloxim, $C : NOC_2H_5$, the formation of which from silver fulminate, $C : NOAg$, and ethyliodide is self-evident. The formation of ethylcyanate, or of its polymer, which is the chief product of the above reaction, is easily explained by an addition of ethyliodide to the unsaturated carbon atom present in silver fulminate,



$$AgON : C + IC_2H_5 = AgON : C\genfrac{}{}{0pt}{}{I}{C_2H_5}.$$

The addition product is then converted by Beckmann's rearrangement into ethylcyanate and silver iodide.

Formation of Ethoxyformamidine, $C_2H_5ON : C\genfrac{}{}{0pt}{}{H}{NH_2}$.

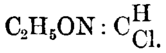
26 grams isuretine were heated, in alcoholic solution, with one molecule of sodium ethylate and ethyliodide (1¼ molecules), for three hours with reversed condenser; the alcohol was thereupon distilled off, and a strong smell of isonitrile and ammonia was noticed. The residue was dissolved in water and repeatedly extracted with ether. After distilling off the ether, and fractionating the liquid remaining, 3 grams of an ethereal weak basic smelling oil were obtained, which boils without decomposition at 170°–175°. Up to the present only 7 grams of this oil have been obtained, which, in view of an analysis of a platinum double salt obtained from it, must be regarded as ethoxyformamidine. It is easily soluble in water; a portion was dissolved in hydrochloric acid, and the evaporated solution taken up in alcohol and treated with platinic chloride. On addition of ether a yellow oil separates out, which, on rubbing with a glass rod, solidifies. The salt was recrystallized from alcohol and ether, and obtained in yellow quadratic plates, melting at 153°

0.3055 gram substance dried at 100° gave 0.1013 gram Pt.

0.3018 gram substance dried at 100° gave 26.6 c.cm. N_2 at 17° and 749 mm.

	Theory for $(C_3H_8N_2O,HCl)_2PtCl_4$.	Found.
Pt	33.16	33.16
N	9.57	10.07

The remaining ethoxyformamidine was dissolved in 4 molecules dilute hydrochloric acid and treated, in the cold, with 1 molecule of sodic nitrite.* A copious evolution of nitrogen is noticed, and after standing for thirty minutes the solution is extracted with ether, and the ethereal solution washed with dilute sodic hydrate and then dried with calcic chloride. An oil is obtained which contains much chlorine, and seems to boil without decomposition, and at higher temperatures possesses a very sharp odor. It is very probable that it consists of ethoximformylchloride,



$$C_2H_5ON : C\genfrac{}{}{0pt}{}{H}{Cl}.$$

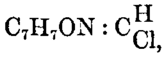
On heating the oil, which is soluble in water, with concentrated caustic alkalies, a strong smell of isonitrile is observed, which can only be due to the formation of ethylcarbyloxime. Ethoximformylchloride seems, however, in comparison with formylchloridoxime, to be remarkably stable, and is split, on treatment with alkalies, chiefly into formic acid, ethoxylamine, and potassic chloride.

The Action of Chloroform and Alcoholic Potash on α Benzylhydroxylamine.

The esters of carbyloxime ought, however, to be obtained most easily from α alkylated hydroxylamines by means of Hofmann's reaction,

$$RONH_2 + CHCl_3 + 3\ KOH = RON : C + 3\ KCl + 3\ H_2O.$$

On adding a mixture of α benzylhydroxamine † (10.4 grams) and chloroform (17.3 grams) to a solution of 19.2 grams potassic hydrate in 70 grams alcohol, an energetic reaction takes place, and a strong smell of isocyanide is noticed. Benzylcarbyloxime, $C_7H_7ON : C$, has, however, been formed only in minute quantities, and 7 grams unchanged α benzylhydroxylamine were recovered. The reason for this seems to me to be due to the fact that the intermediate product,



$$C_7H_7ON : C\genfrac{}{}{0pt}{}{H}{Cl},$$

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* Tiemann and Krüger, Ber. d. chem. Ges., XVIII. 1732.

† Behrend and Leuchs, Ann. Chem. (Liebig) 257, 205.

which must be formed in the reaction,[*] is very stable, just as is the case with ethoximformylchloride mentioned above, and therefore it is split chiefly into α benzylhydroxylamine, formic acid, and potassic chloride.

In the above work on bivalent carbon, which will be continued in various directions, I have been assisted with great skill and with remarkable perseverance by Dr. M. Ikuta, to whom I wish also here to express my warmest thanks.

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[*] Ann. Chem. (Liebig), CCLXX. 308.

VII.

ON THE PROPERTIES OF BATTERIES FORMED OF CELLS JOINED UP IN MULTIPLE ARC.

By B. O. Peirce.

Presented May 9, 1894.

If three galvanic cells the electromotive forces of which are e_1, e_2, and e_3 respectively, and the internal resistances, b_1, b_2, and b_3, be joined up parallel to each other, the battery thus formed is equivalent — so far as its ability to send electricity through an external circuit is concerned — to a single cell of electromotive force e_0, and of internal resistance b_0, where

$$e_0 = \frac{e_1 b_2 b_3 + e_2 b_1 b_3 + e_3 b_1 b_2}{b_2 b_3 + b_3 b_1 + b_1 b_2}, \quad b_0 = \frac{b_1 b_2 b_3}{b_2 b_3 + b_1 b_3 + b_1 b_2}.$$

A similar statement * may be made about a battery of any number of cells connected in multiple arc. It is evident, however, that the efficiency † of such a battery of unlike cells is less than that of a single cell which would do the same amount of useful work under the same external circumstances.

I have had occasion of late to consider some relations between the strengths of the currents which pass through the different members of a given battery of unlike cells joined up in multiple arc. Many persons must have used the equations which I found convenient in this work, but I cannot find that any one ‡ has taken the trouble to print them all. I therefore give a few of them here, with some well known formulas introduced for the sake of clearness.

Let the internal resistances of n cells, which are joined up in multiple arc with each other and with a conductor of resistance r, be b_1, b_2, b_3 . . . respectively, and the electromotive forces be e_1, e_2, e_3 . . .

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* Stepanoff, Journal Russ. Phys. Chem. Soc., XII. 38.

† Slouginoff, Journal Russ. Phys. Chem. Soc., XIV. 2.

‡ I have not had access to the papers of Messrs. Stepanoff and Slouginoff quoted above.

Let C be the current which flows through the outside resistance r, and let C_k be the current which flows, in the same cyclic direction as C, through the kth cell. Then, if $b_k = \lambda_k\, r$,

$$C = \sum_{k=1}^{k=n} C_k; \tag{1}$$

$$b_k\, C_k + r\, C = r\,(\lambda_k\, C_k + \sum_{p=1}^{p=n} C_p) = e_k. \tag{2}$$

Let the determinant of the coefficients of the C's in the set of n linear equations of which (2) is an example, be denoted by Δ_n; then

$$\Delta_n = r^n \begin{vmatrix} 1+\lambda_1 & 1 & 1 & 1 & \cdots & \cdots \\ 1 & 1+\lambda_2 & 1 & 1 & \cdots & \cdots \\ 1 & 1 & 1+\lambda_3 & 1 & \cdots & \cdots \\ 1 & 1 & 1 & 1+\lambda_4 & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & 1+\lambda_n \end{vmatrix}$$

or

$$\Delta_n = r^n\, \delta_n\,.$$

It is evident that δ_{n+1} would be equal to the product of λ_{n+1} and δ_n plus the product of all the λ's from λ_1 to λ_n.

Let M_n represent the product of all the b's.

Let N_n represent the sum of the n products of the b's taken $n-1$ at a time.

Let $P_{n.k}$ represent the sum of the $n-1$ products formed of all the b's except b_k taken $n-2$ at a time.

Let Q_n represent the sum of the n products formed by multiplying every e by all the b's except its own.

Let $S_{n,k}$ represent the sum of the products obtained by multiplying every electromotive force except that of the kth cell by all the b's except its own and b_k.

Then

$$\Delta_n = M_n + r\, N_n. \tag{3}$$

The determinant formed from the determinant of the coefficients (Δ_n) of the C's in the n linear equations of which (2) is a type, by substituting the corresponding e's for the elements of the kth column shall be called $\Delta_{n,k}$.

$$\Delta_{n,k} = \frac{e_k\,(M_n + b_k\,r\,P_{n,k}) - r\,b_k\,S_{n,k}}{b_k}. \tag{4}$$

Hence,

$$C_k = \frac{e_k\,(M_n + b_k r\,P_{n,k}) - r\,b_k\,S_{n,k}}{b_k\,(M_n + r\,N_n)}. \tag{5}$$

The current in the kth cell may be positive, zero, or negative according to circumstances. If the electromotive forces and the internal resistances of all the cells are given, C_k will be positive if r be made less than $\dfrac{e_k\,M_k}{S_{n,k} - e_k\,P_{n,k}}$.

The currents in all the cells will be positive if r be made sufficiently small. If the electromotive forces of the cells are unequal, and if r is very large, the currents in the weakest cell or cells will be negative. If the outside conductor be removed so that the poles of the battery are not connected externally, the current in the kth cell will be positive if e_k is greater than $S_{n,k} \div P_{n,k}$. Thus, if the battery consists of three unlike cells numbered in order of descending electromotive force, C_1 must be positive and C_3 negative, but C_2 will be positive or not according as e_2 is or is not greater than $\dfrac{e_1\,b_3 + e_3\,b_1}{b_1 + b_3}$.

The case of a number of cells of the same internal resistance but of different electromotive forces joined up in multiple arc is of some interest when one has to use a number of unequally charged storage cells to send a very heavy current through an outside circuit of extremely low resistance. When the b's are all equal,

$$C_k = \frac{e_k(b + n\,r) - r\,\Sigma\,(e)}{b\,(b + n\,r)} \quad \text{and} \quad C = \frac{\dfrac{\Sigma\,e}{n}}{\dfrac{b}{n} + r};$$

so that the equivalent cell has an electromotive force equal to the average of the electromotive forces of the given cells, and an internal resistance equal to $\frac{1}{n}$th of that of each cell. This case also throws some light on the properties of a thermal junction of large area formed of two plates of metal soldered together flatwise when, as is sometimes the case in practice, it is impossible to keep the whole junction at exactly the same temperature.

Equations (1) and (5) give the equation

$$C = \frac{\Sigma\left(\frac{e_k}{b_k}\right)}{1 + r\,\Sigma\left(\frac{1}{b_k}\right)} = \frac{\frac{Q}{N_n}}{\frac{M_n}{N_n} + r}, \tag{6}$$

which defines Stepanoff's equivalent cell * already mentioned. The difference of potential between the poles of the battery is

$$V = \frac{r\,Q}{M_n + r\,N_n} \tag{7}$$

When r is made to increase indefinitely, V approaches as a limit the electromotive force Q / N_n of the equivalent cell, and C_k approaches $\frac{e_k\,P_{n,k} - S_{n,k}}{N_n}$, the current in the kth cell when the poles of the battery are not connected by any external conductor.

If there is a battery of electromotive force E in the external circuit, r, the quantity E must, according to the direction of this external electromotive force, be added to or subtracted from the second member of each of the equations of which (2) is an example. If a battery of n cells joined up in multiple arc be itself connected up parallel with a cell of electromotive force E and of internal resistance B, $E \div B$ must be added to the numerator of the fraction which forms the second member of (6), and $r \div B$ to the denominator. Upon an examination of these cases, it appears that, if a battery of cells joined up in multiple arc be itself connected up parallel or in series with another battery, or if it be used for compensation purposes, it will exert the same influence upon the currents and differences of potential in parts of the circuit external to itself as its equivalent cell would exert.

The internal work done in the battery when its poles are connected by the external resistance, r, is

$$W_i = \sum_{k=1}^{k=n} (C_k^2\,b_k). \tag{8}$$

The internal work done in the equivalent cell would be

$$W_i' = \frac{M_n}{N_n}\left[\sum_{k=1}^{k=n} (C_k)\right]^2. \tag{9}$$

Let w be the difference between W_i and W_i', and in the equation found by subtracting the members of (9) from the corresponding mem-

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* See also Slouginoff, Carl's Repertorium, XVI. 539.

bers of (8), let $e_k - Cr$ be substituted for its equal $C_k\, b_k$. It will then be found that all the terms which contain r disappear, since the coefficients of Cr and of $C^2 r^2$ vanish identically, and that

$$w = \frac{M_n}{N_n} \sum_{k=1}^{k=n} \frac{(e_k - e_j)^2}{b_k\, b_j}; \tag{10}$$

where the sign of summation introduces once only every value of $(e_k - e_j)^2$, in which k is different from j, and neither k nor j is greater than n.

Since w does not involve r, it (w) is the work done inside the battery when its poles are not connected by any external resistance. Equation 10 shows that w cannot be negative, and that it is different from zero unless all the cells in the battery have equal electromotive forces. The expression for w may be written in a form due to Slouginoff,

$$w = \sum_{k=1}^{k=n} \left(\frac{e_k^{\,2}}{b_k}\right) - \frac{e_0^{\,2}}{b_0}, \tag{11}$$

where e_0 and b_0 are the electromotive force and the internal resistance respectively of the equivalent cell.

It is known that if the poles of a battery formed of n cells be connected by an outside resistance r, the current in the external circuit will be the same, whether the cells be joined up in series or in multiple arc, provided that

$$r = \frac{Q_n\, \Sigma\, (b_k) - M_n\, \Sigma\, (e_k)}{N_n\, \Sigma\, (e_k) - Q_n}; \tag{12}$$

or, if the cells are all alike, provided that $r = b$. It is worthy of notice, however, that the efficiencies of the battery are different in the two cases. If the cells are joined up in series, the efficiency of the battery is

$$F_s = \frac{r}{r + \Sigma\, (b_k)},$$

but if they are joined up in multiple arc the efficiency is

$$F_p = \frac{C^2\, r}{C^2 r + \Sigma\, (C^2_{\ k}\, b_k)};$$

so that

$$\frac{F_s}{F_p} = \frac{C^2 r + \Sigma\, (C^2_{\ k}\, b_k)}{C^2 r + C^2\, \Sigma\, (b_k)}. \tag{15}$$

If the cells are all alike, and if $r = b$, this ratio has the value $1 \div n$, and the arrangement in parallel is n times as efficient as the arrangement in series. In the case of unlike cells, if the currents in the cells are all positive, F_s is always less than F_p. It is easy, however, to find cases where F_p is less than F_s, for this is true when

$$\Sigma\,(C^2_k\, b_k) < [\Sigma\,(C_k)]^2 \,.\, \Sigma\,(b_k).$$

CAMBRIDGE, July, 1894.

VIII.

CONTRIBUTIONS FROM THE ZOÖLOGICAL LABORATORY OF THE MUSEUM OF COMPARATIVE ZOÖLOGY, UNDER THE DIRECTION OF E. L. MARK, XLII.

ON THE CELL LINEAGE OF THE ASCIDIAN EGG.

A PRELIMINARY NOTICE.

By W. E. Castle.

Communicated by E. L. Mark, June 14, 1894.

The following paper is based on an uncompleted study of the early stages in the development of *Ciona intestinalis*, the material for which I was enabled to collect at the Newport Marine Laboratory in the summer of 1893, through the kindness of Mr. Alexander Agassiz.

Tunicate embryology has been studied from the standpoint of cell lineage to a greater or less extent, by Van Beneden et Julin ('84), Seeliger ('85), and Chabry ('87). The first named authors have followed the segmentation of the egg of *Clavelina Rissoana* as far as the 32-cell stage in a manner that admits of no question as to its accuracy. Every cell division is evidenced by karyokinetic figures that prove beyond doubt the actual genetic relationship.

The cell lineage of a single additional stage is given, one of forty-four cells. This stage must have been derived from the preceding by twelve cell divisions, six in each of the equivalent halves of the egg. Of these six, three are clearly indicated by spindles in the 32-cell stage. The other three were apparently determined by conjecture, and it is my purpose to show that by yielding themselves to conjecture in so small a matter as these three cell divisions, the eminent authors fell into an error which invalidates the most important conclusions of their otherwise excellent work. For in correlating the 44-cell stage with the 32-cell stage they have changed the orientation, so that they have identified the dorsal side of one with the ventral side of the other, the endodermal half of one with the ectodermal half of the other. *Their orientation of all the stages prior to the 44-cell stage* *is accordingly wrong. Their terms ectodermal and endodermal. ventral and dorsal, as employed up to this stage, must be interchanged.*

I shall in the present paper reproduce the figures of the 32-cell and 44-cell stages given by Van Beneden et Julin, with the proper orientation and the probable cell lineage as inferred from that actually determined in Ciona.

Chabry, in a paper concerned chiefly with teratology, traces the cell lineage of *Ascidiella aspersa* to a stage with thirty-two cells, and finds it identical, cell for cell, with that of Clavelina as given by Van Beneden et Julin. He however adopts, apparently without question, the orientation given by them, and makes accordingly, in his early stages the same error, calling dorsal (endodermal) that side of the egg which is really ventral (ectodermal).

He gives in part the cell lineage of the ectodermal side of a single older stage, in which five additional divisions are represented as having occurred in each of the equivalent halves of the egg. (See his Fig. 20.) These agree exactly with the divisions I have found occurring in Ciona subsequent to the 32-cell stage.

Seeliger studied an undetermined species of *Clavelina*, the same genus on which Van Beneden et Julin worked. It has been more than once observed by writers on tunicate embryology, that, though engaged with the study of forms so nearly related, these authors differ widely in their conclusions.

In discussing the 4-cell stage, for example, Van Beneden et Julin state that the two larger cells give rise to the anterior portion of the embryo, and in this I fully agree, whereas Seeliger contends that they produce the posterior portion. Seeliger however gives little evidence in support of his view, for his determination of the cell lineage is in most cases so manifestly a matter of mere conjecture that it hardly merits a serious consideration. But it may be worth while to point out where he has made the mistake that led to his false conclusion. It is in passing from the 16-cell stage to the next succeeding stage, the number of cells in which he did not take the pains to determine. In doing this he has reversed the poles anterior and posterior. For his 16-cell stage (his Figs. 14 and 15), *if its anterior and posterior poles be reversed*, corresponds unmistakably, both in the characteristic arrangement of its cells and in their relative size, with the 16-cell stage figured by Van Beneden et Julin (their Figs. 8 and 8a), and that figured by Chabry (his Figs. 17 and 24), and I can add from my own observations that it also corresponds with that of Ciona.

Seeliger's next stage (his Fig. 16) is oriented correctly, the posterior end being clearly indicated by the smaller marginal cells (left unshaded in his figure). This criterion for the posterior end of the embryo had been previously pointed out by Van Beneden et Julin, has since been recognized by Chabry and by Davidoff for the forms they studied, and holds good for Ciona also.

Seeliger speaks of his Figure 16 as representing a stage with fourteen "endoderm" cells (that is, cells which have been derived from the four dorsal cells of the 8-cell stage). It is highly probable that he should have represented as "endodermal" also a pair of lateral marginal cells left unshaded in his figure, thus bringing the number of descendants of the four dorsal cells of the 8-cell stage up to sixteen, the number we should expect as the result of two successive divisions in that hemisphere. The two cells in question correspond in position with the cells $c^{6.5}$ and $d^{6.5}$ of Figure 4 of this paper, except that in the egg of Ciona figured the cells named do not reach the margin, but lie a little more central.

Interpreted thus, Seeliger's Figure 16 corresponds closely with a similar view of the 32-cell stage of Van Beneden et Julin (reproduced in Figure 8 of this paper), and with Chabry's Figure 26, and with the same stage of Ciona (Figure 4 of this paper).

From this stage on, all investigators are agreed as to which is the anterior and which the posterior end of the embryo. If then the orientation of Seeliger's later stages is correct (and this will be conceded by every one), that of his 16-cell stage is *in*correct; and unless he again reversed the poles in passing from the 4-cell to the 16-cell stage, his *4-cell stage is also wrongly oriented.* This being so, the two larger cells of the 4-cell stage are really anterior in the Clavelina studied by Seeliger, just as in the one studied by Van Beneden et Julin.

Another point of difference between the authors mentioned, appears in their discussion of the 8-cell stage. Seeliger states that the larger cells belong to the ventral (ectodermal) half of the egg, whereas Van Beneden et Julin state that they constitute the dorsal (endodermal) half.

I shall presently show that Van Beneden et Julin were mistaken in their determination of the dorsal and ventral faces of the 32-cell and earlier stages. It follows that the larger cells, which they called *dorsal*, were really *ventral*, as stated by Seeliger for the form studied by him. If this is so, another point of difference is removed, for in both the species of Clavelina that have been studied the larger cells of the 8-cell stage are ventral with reference to the axes of the future larva.

In any extended work on cell lineage it is desirable to have some system of naming the individual cells which will indicate readily the exact history of each, — from what part of the matured ovum it has been derived, by how many divisions it is removed from the ovum, and from what other cells these divisions have separated it.

What system one adopts is a matter of choice, but not of indifference. Chabry has employed a fairly good one in his work on Ascidiella. It is too cumbersome, however, for advanced stages, and limited in its applicability. Van Beneden et Julin have simply employed numerals, which give no information whatever as to the derivation of cells. Seeliger has followed no system at all beyond the 16-cell stage, except that of arrows joining cells of the same parentage, which serves to mark the lineage for only one generation.

So far as I know, only one system capable of general application to different types of cleavage has been proposed, that introduced by Kofoid ('94) in his recent work on Limax. As this seems to me to embody several distinct advantages over other systems, I shall follow its general features in this paper.

1. Each cell will be designated by a letter with two exponents.

2. The letter indicates the quadrant of the egg from which the cell in question has been derived, or, in other words, that cell of the 4-cell stage from which it is descended. Viewing the egg from the *ventral* or *ectodermal* side, the left anterior quadrant is A, the right anterior B, the right posterior C, and the left posterior D. In dorsal views, right and left are of course reversed.

As the third cleavage plane is equatorial and separates a ventral from a dorsal hemisphere, I shall designate the cells of the former by capitals and those of the latter by small letters.

3. The first exponent indicates the *generation* to which a cell belongs; that is, the number of cell divisions by which it is removed from the unsegmented ovum.

The ovum is generation one, the 2-cell stage two, the 4-cell stage three, etc.

4. The second exponent indicates the *number* of a cell in a generation, the cells of each quadrant being numbered independently of the other quadrants from the centre of the ventral (*ectodermal*) toward the centre of the dorsal side.* If in any case two cells of common de-

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* In this I do not follow Kofoid, who numbers from the ventral (in his case *endodermal*) toward the dorsal (in his case *ectodermal*) pole. His system of nomenclature I have treated throughout as being, for my purposes, not an index to homologies between blastomeres, but a convenient method of notation.

scent lie in an equatorial position, that one which is nearer the median plane will be given the lower numeral.

It will be noted that I follow the accepted usage, orienting the egg with reference to the future axes of the embryo, and using the terms dorsal and ventral in this sense. I have regarded the egg as viewed from the ventral rather than the dorsal side, because, as is rightly held, the ventral side corresponds to the *ectodermal* pole.

Below is a table, the first six columns of which show the complete cell lineage of the right half of the egg of Clavelina, Ascidiella, or Ciona through the sixth generation (32-cell stage). The terminology of Van Beneden et Julin for the 32-cell stage is given in the seventh column, for purposes of comparison. In the next column is given, in

Cell Lineage of the egg of Clavelina, Ascidiella, or Ciona, right half only, through the 32-cell stage.						CLAVELINA.				
						Terminology of V. B. et J.	Interpretation of V. B. et J.			My Interpretation.
							Their Terminology.		My Terminology.	
First Gen.	Second Gen	Third Gen.	Fourth Gen.	Fifth Gen.	Sixth Gen.	Sixth Gen.	6th, 7th, and 8th Gen.		6th, 7th, and 8th Gen.	6th & 7th Gen.
$\overline{ABCD}^1$	$\overline{AD}^2$	A^3	$A^{4\cdot1}$	$A^{5\cdot1}$	$A^{6\cdot1}$	XIV		20	$A^{7\cdot1}$	$a^{6\cdot6}$
								14	$A^{7\cdot2}$	$a^{6\cdot5}$
					$A^{6\cdot2}$	1		1	$A^{6\cdot2}$	$A^{6\cdot2}$
				$A^{5\cdot2}$	$A^{6\cdot3}$	XV		21	$A^{7\cdot5}$	$a^{6\cdot8}$
								15	$A^{7\cdot6}$	$a^{6\cdot7}$
					$A^{6\cdot4}$	10		10	$A^{6\cdot4}$	$A^{7\cdot8}$
			$a^{4\cdot2}$	$a^{5\cdot3}$	$a^{6\cdot5}$	2		2	$a^{6\cdot5}$	$A^{7\cdot2}$
					$a^{6\cdot6}$	3		3	$a^{6\cdot6}$	$A^{7\cdot1}$
				$a^{5\cdot4}$	$a^{6\cdot7}$	9		9	$a^{6\cdot7}$	$A^{7\cdot7}$
					$a^{6\cdot8}$	4		4	$a^{6\cdot8}$	$A^{7\cdot5}$
		D^3	$D^{4\cdot1}$	$D^{5\cdot1}$	$D^{6\cdot1}$	XVI	XVI*	22	$D^{8\cdot1}$	$d^{6\cdot8}$
								16	$D^{8\cdot2}$	$d^{6\cdot7}$
							19	19	$D^{7\cdot2}$	$D^{6\cdot3}$
					$D^{6\cdot2}$	XIII		13	$D^{7\cdot3}$	$d^{6\cdot6}$
								18	$D^{7\cdot4}$	$D^{7\cdot4}$
				$D^{5\cdot2}$	$D^{6\cdot3}$	7		7	$D^{6\cdot3}$	$D^{7\cdot2}$
					$D^{6\cdot4}$	VIII		8	$D^{7\cdot7}$	$D^{7\cdot8}$
								17	$D^{7\cdot8}$	$D^{7\cdot7}$
			$d^{4\cdot2}$	$d^{5\cdot3}$	$d^{6\cdot5}$	11		11	$d^{6\cdot5}$	$d^{6\cdot5}$
					$d^{6\cdot6}$	12		12	$d^{6\cdot6}$	$A^{7\cdot6}$
				$d^{5\cdot4}$	$d^{6\cdot7}$	6		6	$d^{6\cdot7}$	$D^{7\cdot1}$
					$d^{6\cdot8}$	5		5	$d^{6\cdot8}$	$D^{7\cdot3}$
	[$\overline{BC}^2$]	(=left half)								
1-cell stage.	2-cell stage.	4-cell stage.	8-cell stage.	16-cell stage.	32-cell stage.	32-cell stage.	44-cell stage.		44-cell stage.	44-cell stage.

the terminology of Van Beneden et Julin, the cell lineage of the 44-cell stage *as interpreted by them;* and in the succeeding column this interpretation is repeated in terms of the nomenclature adopted by me. Finally, in the last column is given *my own interpretation* of the same stage.

The cell lineage for the left half of the egg would be expressed by substituting, in the table, B, b, for A, a, and C, c, for D, d, where my terminology is used; and where the terminology of Van Beneden et Julin is used, by adding a (′) to each of the numerals.

To ascertain the designation of the mother cell of any particular cell, its *first* exponent must be diminished by one; and its *second* exponent, if an even number, must be divided by two, but if an odd number it must first be increased by one and then divided by two.

In order to determine the daughter cells of a particular cell, simply reverse this process; that is, increase the first exponent by one and double the second exponent. The result will be the name of the daughter cell having an *even* second exponent. To determine the other daughter cell, diminish this second exponent by one. Thus the daughter cells of $a^{5.4}$ are $a^{6.8}$ and $a^{6.7}$.

This system I have applied to the 32-cell stage of Van Beneden et Julin in Figures 7 and 8, reproduced from their Figures 9 and 9a, the orientation being corrected to agree with my interpretation.

Similar views of the same stage of Ciona are given in Figures 3 and 4.

It will be seen that this stage of Ciona corresponds cell for cell with the one of Clavelina figured.

In both, the posterior end is marked on one side (Figs. 3 and 7) by the superficially, if not actually, largest pair of cells in the egg at this stage, while underneath them, best seen from the other face of the egg, is the smallest pair of cells (Figs. 4 and 8). The only thing in the egg of Ciona figured which is not perfectly typical is the position of the cells $a^{6.5}$ and $b^{6.5}$, which in other specimens examined lie anterior quite as often as lateral to their sister cells, $a^{6.6}$ and $b^{6.6}$ respectively.

A nearly median optical section parallel to the sagittal plane of the egg exhibited in Figures 7 and 8 is reproduced in Figure 13, and an actual transverse section of the same stage of Ciona is represented in Figure 15. It will be seen that in both cases the cells of one face, which are apparently very large when viewed from the surface, are really thin and superficial; while the apparently small cells of the other face are really high, columnar, and of considerable volume.

These figures leave no doubt that the view of the Ciona egg given in Figure 3 corresponds with that of the egg of Clavelina given in Figure 7, and that the view of the Ciona egg given in Figure 4 corresponds with the view of the Clavelina egg given in Figure 8. If then it can be shown by a detailed study of later stages that the orientation given for the egg of Ciona in Figures 3 and 4 is the correct one, it follows that the orientation given for the egg of Clavelina in Figures 7 and 8 is also correct, and that the orientation given to this stage by Van Beneden et Julin is consequently wrong; for they call Figure 7 a dorsal, and Figure 8 a ventral view.

An examination of Figure 3 shows that the thin superficially large cells seen in this view of the egg are preparing for division. These, as the lettering indicates, are derived from the four ventrally situated cells of the 8-cell stage, and will be referred to collectively as the *ventral* or *ectodermal* half of the egg. The latter term must not be understood, however, to imply that all the cells derived from this hemisphere become ectoderm, but merely that ectoderm is its principal derivative.

The other half of the egg, composed of high, columnar cells, will be called the *dorsal* or *endodermal* half of the egg, with the same restriction on the term endodermal as has been made for ectodermal.

Figure 4 shows the cells of the endodermal half to be quiescent, while those of the ectodermal half are preparing for division. A similar acceleration in division of the ectodermal over the endodermal half of the egg was to be observed at the 24-cell stage (Figs. 1 and 2). Here the cells of the ectodermal half are seen to have passed into the sixth generation, while the cells of the endodermal half are only in the spindle stage, preparatory to the division which will carry them into that generation.

Figure 5 represents a ventral view of a stage of forty-six cells, and shows accomplished the divisions foreshadowed in Figure 3. All the cells of the ventral half of the egg, except the pair of small posterior cells, have divided either completely or partially, thus passing into the seventh generation. I should add that no one of the divisions indicated is a matter of inference, but spindles have been observed in every instance; where they were not to be seen in the specimen figured, they have been observed in other specimens not quite so advanced in development.

Figure 6 gives a view of the opposite face of the same egg. The cells of the dorsal half are here seen to be in the sixth generation, and still quiescent. In a single cell, $b^{6.5}$, a pair of astral radiations it visible. This fact does not, however, foreshadow an *immediate* division of the cell, as these radiations often exist some time before the division actually occurs. It does indicate, however, as the sequel will show, that this cell with its mate, $a^{6.5}$, will be among the earliest cells of the endodermal half of the egg to divide.

In Figures 9 and 10 are reproduced Van Beneden et Julin's figures of the 44-cell stage of Clavelina (their Figs. 10 and 10a). The lettering on the *left* half of Figure 9 and the *right* half of Figure 10 indicates what I believe to be the correct interpretation of the cell lineage of this stage. The interpretation of Van Beneden et Julin is indicated (in terms of my own nomenclature) on the *right* half of Figure 9 and the *left* half of Figure 10.*

It will be seen that at this stage, according to my interpretation, exactly the same divisions, with one exception, have occurred in the egg of Clavelina as in the Ciona egg shown in Figures 5 and 6. The exception mentioned is in the case of the most anterior cell of the ectodermal half, on each side of the median plane ($A^{6.2}$ and its mate, Figs. 8 and 9). This cell has not yet divided, but has remained in the sixth generation, whereas in Ciona it has given rise to $A^{7.3}$ and $A^{7.4}$.

Not only has division occurred in corresponding cells in the egg of Clavelina and that of Ciona, but this division has taken place in the same direction in every instance.

There is, however, in the two eggs, a slight difference in the arrangement of the cells resulting from this division, due perhaps to a difference in the order of division. In the egg of Clavelina (Fig. 9, left half), the cells $A^{7.5}$ and $D^{7.3}$ have been pushed toward the median plane so that they are in contact with their mates in the other half of the egg, and separate $A^{7.1}$ from $D^{7.1}$; but in the egg of Ciona (Fig. 5) $A^{7.5}$ and $D^{7.3}$ do *not* reach the median plane, so that $A^{7.1}$ is left in contact with $D^{7.1}$.

Van Beneden et Julin identify the face of the egg represented in Figure 9 with that seen in Figure 8, and that in Figure 10 with the one seen in Figure 7. In doing so they are forced into several very strange correlations. For example, the small posterior cell $C^{6.3}$ of Figure 8 is identified with the rather large cell $D^{7.2}$ of Figure 9; while the real $C^{6.3}$ ($D^{7.2}$ of Fig. 10, left half) is derived from $D^{6.1}$ (Fig. 7), and its sister cell is supposed to have divided again, so that the other derivatives of $D^{6.1}$ ($D^{8.1}$ and $D^{8.2}$ of Fig. 10, left half) are in the *eighth* generation.

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* It will facilitate a comparison with the lettering of the original, if the reader will make use of the table on page 204.

Finally, the nearly median optical section of this egg, reproduced in Figure 14, shows at a glance the absurdity of Van Beneden et Julin's interpretation. Here the relatively large columnar cells $d^{6.7}$, $d^{6.8}$, $a^{6.6}$, and $a^{6.5}$ of my interpretation,* are derived by them from the thin superficial cells $D^{6.1}$ and $A^{6.1}$ of the preceding stage (Fig. 13), the first two together with $D^{6.3}$ as a result of *two successive divisions* of the single cell $D^{6.1}$. On the other hand the small cubical cells $D^{7.1}$, $D^{7.3}$, $A^{7.5}$, $A^{7.1}$, and $A^{7.2}$ are taken by them to represent, *undiminished by division,* the voluminous columnar cells $d^{6.7}$, $d^{6.8}$, $a^{6.8}$, $a^{6.6}$, and $a^{6.5}$ respectively, of the preceding stage.

It is thus seen from an examination of Van Beneden et Julin's own figures, that they have reversed the dorsal and ventral relations in passing from the 32-cell to the 44-cell stage, and have identified the endodermal half of one with the ectodermal half of the other. This fact has been overlooked by all subsequent writers on tunicate embryology, for all have accepted as correct the results obtained by Van Beneden et Julin.

The question next arises, Is the orientation given by Van Beneden et Julin for the 32-cell stage, or that given for the 44-cell stage, the correct one? A strong presumption that the latter is the case exists in the close correspondence in form and size between the endoderm cells of the gastrula figured by them (their Fig. 11d) and the columnar dorsal cells of their 44-cell stage. This presumption becomes as strong as anything except direct observation of Clavelina can make it, when one follows the cell lineage of Ciona through to a stage which marks the beginning of gastrulation, such as I have represented in Figures 11 and 12.

In order to avoid the extension of this paper to an undesirable length, I have not figured the stages intervening between the 46-cell stage and gastrulation. A detailed study of these stages, however, allows me to speak with confidence of the changes which have occurred.

In the 32-cell stage (Figs. 3 and 4), all the cells of both hemispheres were seen to be in the sixth generation, though, as has been stated, the cells of the dorsal half had divided a little later than those of the ventral half. These dorsal cells now remained quiescent, while all the cells of the ventral or ectodermal half, except the small posterior cells $C^{6.3}$ and $D^{6\,3}$, divided, and thus brought about the 46-cell stage. Before the division (Figs. 3 and 4), it will be noted, the cells of the ectodermal half were so arranged that twelve of them were marginal and in contact with cells of the endodermal half, while four ($A^{6.1}$, $B^{6.1}$, $C^{6.1}$, and $D^{6.1}$, Fig. 3) were entirely surrounded by cells of the ectodermal half. These four now divide along planes perpendicular to the sagittal plane, so that both the daughter cells of each still abut on the median plane. All the marginal cells, however, except the small posterior pair, which remains quiescent, divide in such a way that only one of the daughter cells of each is still marginal and in contact with cells of the endodermal half (Fig. 5, $A^{7.4}$, $A^{7.3}$, $A^{7.6}$, $D^{7.4}$, $D^{7.8}$, and the corresponding cells in the right half of the figure).

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* See Explanation of Plates, Figure 14.

The next division again involves those cells of the ectodermal half of the egg which are marginal, including this time the small posterior cells $C^{6.3}$ and $D^{6.3}$, which have lagged one generation behind the other cells of the ectodermal hemisphere, but now give off toward the median plane each a peculiar flattened cell of minute dimensions, undoubtedly the "petites cellules cunéiformes" of Van Beneden et Julin. This division also passes through two other cells of the ectodermal half, $C^{7.7}$ and $D^{7.7}$, and six anterior and marginal cells of the endodermal half, namely, $a^{6.5}$, $a^{6.7}$, $d^{6.5}$, and their mates $b^{6.5}$, $b^{6.7}$, and $c^{6.5}$.

Concomitantly with this division of marginal cells, and to a greater or less extent in consequence of it, the endodermal face of the egg becomes flat, its cells being crowded together at their superficial ends and expanding club-shaped beneath the surface. The ectodermal face at the same time becomes more convex, its cells growing thinner and spreading out so as to cover a greater area. The marginal cells gradually extend around on to the endodermal face, and thus gastrulation begins.

At this stage (66-cell) the ectodermal half of the egg consists of forty-four cells, of which twenty-four, the more marginal ones, are in the *eighth* generation, and the remaining twenty, centrally or posteriorly situated, are in the *seventh* generation.

The endodermal half of the egg, on account of its less rapid cleavage, is composed of fewer cells, viz. twenty-two, just half the number in the ectodermal portion. Of these, twelve — lying anterior and marginal — are in the *seventh* generation, and ten — central or posterior — in the *sixth* generation.

It will thus be seen (1) that the cells of the dorsal half have lagged just one generation behind those of the ventral half, and (2) that cell division has been more active in the anterior and lateral marginal portions of the egg. As a consequence of the first mentioned fact, a gastrula is formed with a dorsal blastopore by a process "intermediate between epibole and invagination"; and because of the second, the blastopore closes from the sides and anterior end, so that it ultimately becomes pear-shaped and lies in the posterior half of the embryo.

The part which particular cells take in forming the organs of the larva is reserved for discussion in a later paper, as that part of my work is still incomplete. One thing may, however, be stated positively. The entire endoderm and mesoderm are *not* derived as stated by Van Beneden et Julin from the twelve cells of the 44-cell stage, $a^{6.5}$, $a^{6.6}$, $a^{6.7}$, $a^{6.8}$, $d^{6.7}$, $d^{6.8}$, $b^{6.5}$, $b^{6.6}$, $b^{6.7}$, $b^{6.8}$, $c^{6.7}$, and $c^{6.8}$.

CONCLUSIONS.

1. The conflicting statements of Van Beneden et Julin on the one hand, and Seeliger on the other, regarding the segmentation of the ascidian egg, are explained by the detection of a fundamental error in the work of each.

Seeliger has determined the dorsal and ventral sides of the egg correctly, but reversed the anterior and posterior ends in all his figures of the early stages. Van Beneden et Julin have determined correctly the anterior and posterior ends, but have reversed dorsal and ventral in all stages previous to the 44-cell stage. These errors are clearly indicated by a critical examination of the authors' own figures, and a careful study of the cell lineage of Ciona leaves no doubt of their existence.

2. The correction of Van Beneden et Julin's unfortunate change of orientation necessitates fundamental changes in their conclusions.

(*a*) It is stated by them that the four smaller cells of the 8-cell stage give rise to ectoderm only, while the four larger cells produce both endoderm and ectoderm. On the contrary, neither the four smaller cells nor the four larger ones produce *ectoderm* exclusively; but it is the four larger, not the four smaller ones, which give rise to the greater portion, perhaps all, of the ectoderm.

(*b*) I cannot at present assent to the statement of Van Beneden et Julin that the separation of the germ layers is complete at the 44-cell stage.

3. In *Ciona*, from the sixth to the eighth generations at least, cell multiplication is *more* rapid in the anterior and lateral portions of the egg, and this fact is an important element in determining the shape and position of the gastrula mouth.

CAMBRIDGE, May 9, 1894.

POSTSCRIPT.

Since the foregoing was written I have had the opportunity of making further observations upon the living egg of Ciona immediately after fertilization and during the early stages of segmentation. I have repeatedly seen the polar globules and observed continuously the cleavage stages following their formation. These observations lead to the surprising but unavoidable conclusion, that the point on the surface of the egg at which the polar globules form becomes later the centre of the *dorsal* or *endodermal* half of the egg. The evidence for this conclusion will be presented and its significance discussed in a future paper.

September 29, 1894.

POSTSCRIPT NO. 2.

After the preceding was already in print, Paul Samassa's recent paper was received (Zur Kenntniss der Furchung bei den Ascidien. Arch. f. mik. Anat., Bd. XLIV. Heft I. pp. 1-14, Taf. I. und II. Ausgegeben 15 Sept., 1894).

Samassa's conclusions agree in a gratifying manner with my own, that Van Beneden et Julin on the one hand, and Seeliger on the other, were mistaken in their orientation of the Ascidian egg. Here, however, the agreement ends, for my own interpretation of the cell lineage differs radically from that of Samassa.

In the earlier part of this paper I have pointed out how fatal to the conclusions of Van Beneden et Julin was their *conjecture* as to the manner of division in only three pairs of cells in the egg of Clavelina. I cannot forbear saying that a more apt illustration of the utter untrustworthiness of this method of determining cell lineage could not have been offered than is found in Samassa's paper, where the method of conjecture seems to have been followed in a wholesale and entirely unjustifiable manner.

In his account of the 32-cell stage Samassa makes $D^{6.1}$ (his c 11) the sister cell of $D^{6.3}$ (his c 12) both in Ciona and in Clavelina. In doing so he contradicts, though without giving a particle of evidence in support of his views, the recorded observations of Van Beneden et Julin on Clavelina and of Chabry on Ascidiella, and this too in the face of the fact that Van Beneden et Julin offer the absolutely incontrovertible evidence of karyokinetic figures in support of their interpretation.

In the living egg of Ciona I have myself repeatedly seen the cell divisions leading to the 32-cell stage take place, and my observations agree perfectly with those of Van Beneden et Julin on Clavelina, and of Chabry on Ascidiella, viz. that the cell $D^{6.1}$ (Samassa's c 11) is the sister cell of $D^{6.2}$ (Samassa's c 21) and $D^{6.3}$ (c 12) that of $D^{6.4}$ (c 22). If Samassa expects his statement to stand against all these independent observations, he must present some evidence in its support.

After discussing the 48-cell stage of Ciona, Samassa says: "Die weiteren Theilungen habe ich nicht Zelle für Zelle verfolgt, da dies für die Lösung der mich interessirinder Frage nicht von Bedeutung ist." Yet, again without a particle of evidence and confessedly without detailed observations, he calmly proceeds to declare the *ancestry* and *fate* of the individual blastomeres of subsequent stages! The history *cell for cell* of the cleavage subsequent to the 48-cell stage is *precisely* the *critical* point in deciding the question with which Samassa is concerned, viz. the origin of the endoderm, and in stopping where he did he has stopped short of solving his problem. Worse than this, by his guesses at the cell lineage he has fallen into positive error. For example, the cells 8 and 9 of his Figure 10, which he says are *ectoderm*, are not so at all, but are *mesoderm*. They with their mates in the left half of the egg ultimately form the greater part, perhaps all, of the longitudinal musculature of the tail, being derived from cells corresponding to $D^{8.16}$ and $d^{6.6}$ of my Figure 12. There is no mistaking the identity of these cells; the large size of the nucleus, which Samassa has observed for his cell 8, and would have found to hold good at a slightly different stage for 9 also, is one of their distinguishing characteristics; their peculiar stainability under proper treatment is another. Samassa assures us that these cells are derived from the ventral or ectodermal cells of the 8-cell stage, and represent, with a few cells posterior to them, "die erste Anlage der Medullarwülste." With these statements I squarely take issue. Of those under consideration, only the cell 8 (my $D^{8.16}$) with its mate in the left half of the egg, is derived from the ventral cells of the 8-cell stage, the other cell (9) is derived from the dorsal cells of the 8-cell stage; and *both* 8 and 9 form, not *ectoderm*, but *mesoderm*, being invaginated with the endoderm cells at gastrulation.

In view of these facts, and others which need not be presented at this time, I am forced to take issue with Samassa's main conclusion, "dass bei Ciona und Clavelina durch die dritte Furchung die Trennung der beiden primären Keimblätter erfolgt." For Ciona at least this is *not* true, and the close correspondence which Samassa himself has recognized between the early stages of Ciona and those of Clavelina renders its occurrence in Clavelina *exceedingly improbable.*

Davidoff's belief that the first equatorial cleavage separated the two primary germ layers can have no weight one way or the other in deciding the question, for Davidoff did not profess to have traced cell by cell the history of the cleavage subsequent to the 8-cell stage.

If my statements in this Postscript seem to the reader to be as dogmatic as Samassa's, I can only say that they rest, not on confessed inference or conjecture as to the cell lineage, but on repeated observations made on *dozens* of embryos, only *continuous observations of the living egg* or *the presence of karyokinetic figures* in preserved specimens being admitted as sufficient evidence of the genetic relationships of cells. The evidence afforded by my figures will be presented, and a more exhaustive discussion of the subject made, in a subsequent paper.

October 5, 1894

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EXPLANATION OF PLATES.

Arrows joining cells indicate divisions that have occurred since the last stage figured or described.

A = Anterior. P = Posterior. R = Right. L = Left. D = Dorsal. V = Ventral. For the system of lettering employed to indicate cell lineage, consult the text, pp. 203, 204.

PLATE I.

Ciona intestinalis.

All the figures of this plate are drawn to the same magnification, 400 diameters.

Figure 1. Egg of Ciona, 24-cell stage, ventral view. The cells of the ventral half of the egg number sixteen, and are all in the sixth generation. The most recent division is seen to have been that resulting in the posterior cells $D^{6.3}$, $D^{6.4}$, and $C^{6.3}$, $C^{6.4}$.

" 2. The same egg, dorsal view. The cells of the dorsal half of the egg are still in the fifth generation, and consequently number only eight. They are, however, about to divide, and the spindles indicate the directions in which divisions will occur.

" 3. Egg of Ciona, 32-cell stage, ventral view. (Divisions which were already completed at the 24-cell stage are again indicated by arrows, for convenience in comparison.)

" 4. The same egg, dorsal view.

" 5. Egg of Ciona, 46-cell stage, ventral view. All the cells of the ventral half of the egg are seen to have divided more or less completely since the 32-cell stage, except the small posterior cells $C^{6.3}$ and $D^{6.3}$.

" 6. The same egg, dorsal view. All the cells of the dorsal half of the egg are still in the sixth generation, as in Figure 4.

Fig. 1.

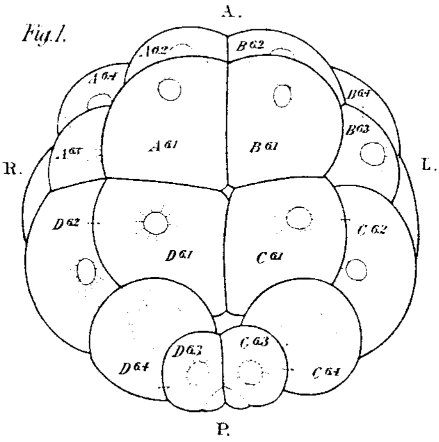

A.
A 6.2
B 6.2
A 6.4
B 6.4
B 6.3
A 6.3
A 6.1
B 6.1
R.
L.
D 6.2
C 6.2
D 6.1
C 6.1
D 6.3
C 6.3
D 6.4
C 6.4
P.

Fig. 2.

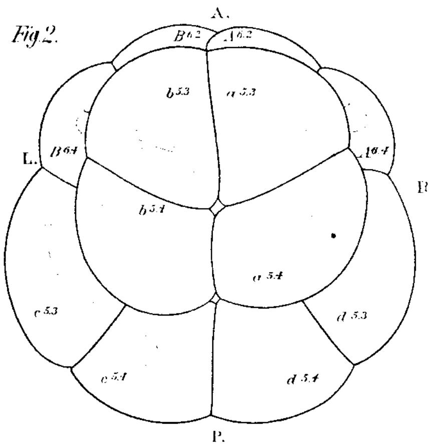
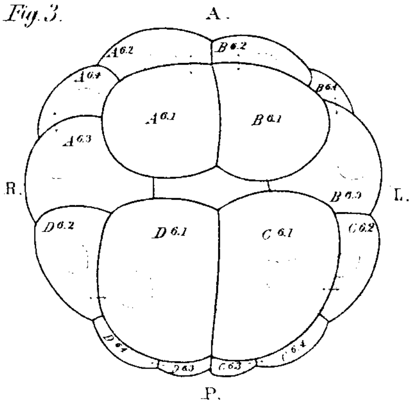

A.
B 6.2
A 6.2
b 5.3
a 5.3
L.
B 6.4
A 6.4
R.
b 5.4
a 5.4
c 5.3
d 5.3
c 5.4
d 5.4
P.

Fig. 3.


A.
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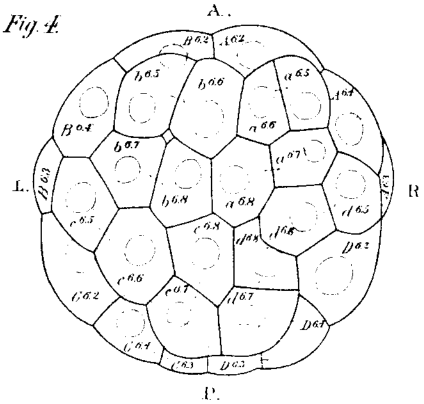
B 6.2
A 6.4
B 6.4
A 6.1
B 6.1
A 6.3
R.
B 6.3
L.
D 6.2
D 6.1
C 6.1
C 6.2
D 6.4
C 6.4
D 6.3
C 6.3
P.

Fig. 4.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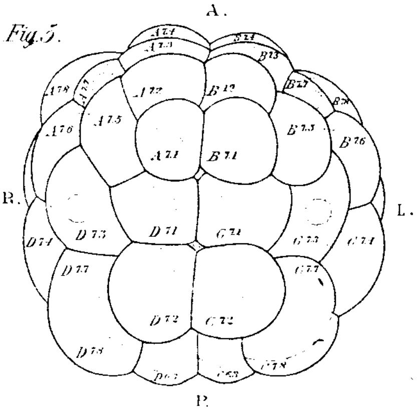
b 6.6
a 6.5
A 6.4
B 6.4
a 6.6
b 6.7
a 6.7
L.
B 6.3
b 6.8
a 6.8
d 6.5
A 6.3
R.
c 6.5
c 6.8
d 6.8
d 6.6
D 6.2
c 6.6
C 6.2
c 6.7
d 6.7
D 6.4
C 6.4
C 6.3
D 6.3
P.

Fig. 5.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B 7.4
B 7.3
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A 7.7
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B 7.2
B 7.7
B 7.8
A 7.6
A 7.5
B 7.5
B 7.6
A 7.1
B 7.1
R.
L.
D 7.4
D 7.3
D 7.1
C 7.1
C 7.3
C 7.4
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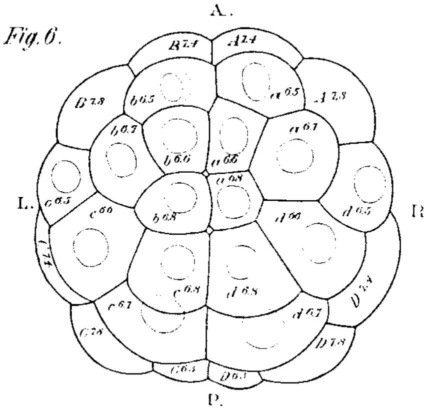
D 7.8
D 6.3
C 6.3
C 7.8
P.

Fig. 6.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a 6.5
A 7.8
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a 6.7
b 6.6
a 6.6
a 6.8
L.
c 6.5
c 6.6
b 6.8
d 6.6
d 6.5
R.
C 7.4
c 6.8
d 6.8
D 7.4
c 6.7
d 6.7
C 7.8
D 7.8
C 6.3
D 6.3
P.

PLATE II.

Figures 7, 8, 9, 10, 13, and 14 are copied from Van Beneden et Julin's figures of *Clavelina Rissoana.* The others are of *Ciona;* magnification, 400 diameters.

Figure 7. Egg of Clavelina, 32-cell stage, with corrected orientation, ventral view. (After Van Beneden et Julin's Fig. 9a).

" 8. The same egg, dorsal view. (After Van Beneden et Julin's Fig. 9.)

" 9. Egg of Clavelina, 44-cell stage, ventral view. (After Van Beneden et Julin's Fig. 10.) On the *left* side of the figure is given the corrected cell lineage, on the *right* side, the cell lineage according to Van Beneden et Julin.

" 10. The same egg, dorsal view. (After Van Beneden et Julin's Fig. 10a.) On the *right* side of the figure is given the corrected cell lineage, on the *left,* the cell lineage according to Van Beneden et Julin.

" 11. Egg of Ciona, 66-cell stage, ventral view. Only the marginal cells of the ventral half have divided since the stage shown in Figures 5 and 6.

" 12. The same egg, dorsal view. By more rapid division in the ventral half of the egg certain of its marginal cells have been shoved around on to this face of the egg. Six marginal and anterior cells of the dorsal half have also divided since the 46-cell stage.

" 13. A nearly median optical section, parallel to the sagittal plane, of the egg of Clavelina shown in Figures 7 and 8, with corrected orientation. (After Van Beneden et Julin's Fig. 9c.)

" 14. A nearly median optical section, parallel to the sagittal plane, of the egg of Clavelina shown in Figures 9 and 10. (After Van Benenen et Julin's Fig. 10c.)

" 15. An actual transverse section of an egg of Ciona in the 32-cell stage

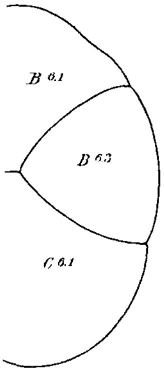
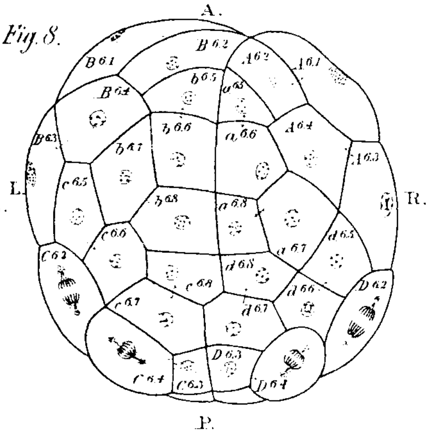

B 6.1
B 6.3
C 6.1
L.

Fig. 8.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B 6.4
b 6.5
a 6.5
B 6.3
b 6.6
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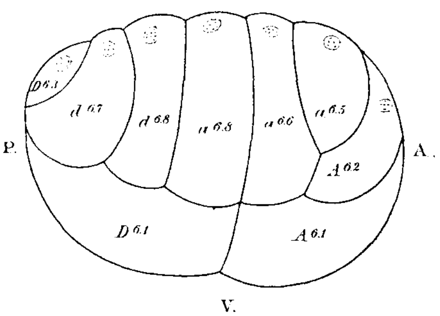
A 6.4
b 6.7
A 6.3
L.
c 6.5
b 6.8
a 6.8
R.
c 6.6
a 6.7
d 6.5
C 6.2
d 6.8
c 6.8
d 6.6
D 6.2
c 6.7
d 6.7
D 6.3
C 6.4
C 6.3
D 6.4
P.

Fig. 13.


D.
D 6.3
d 6.7
d 6.8
a 6.8
a 6.6
a 6.5
P.
A 6.2
A.
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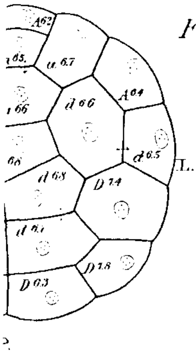
A 6.1
V.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a 6.6
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L.
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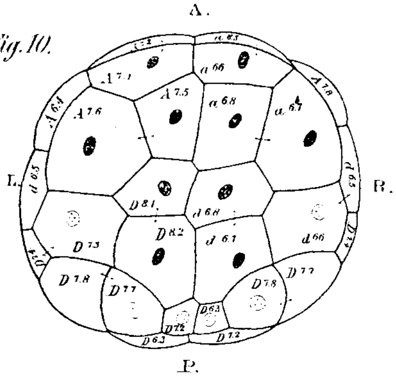
D 6.3
P.

Fig. 10.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a 66
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a 6.8
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L.
d 6.5
d 6.5
R.
D 8.1
d 6.8
D 7.3
D 8.2
d 6.1
d 66
D 7.4
D 7.4
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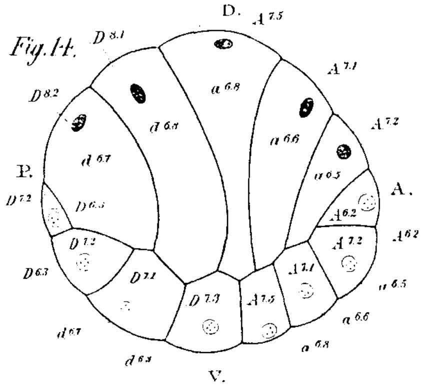
D 6.3
D 7.2
P.

Fig. 14.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A 7.1
D 8.2
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d 6.8
A 7.2
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P.
a 6.5
D 7.2
D 6.3
A.
A 6.2
A 7.2
A 6.2
D 7.2
D 6.3
D 7.1
A 7.1
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D 7.3
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d 6.3
V.

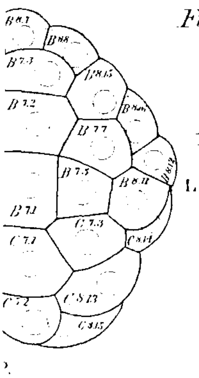
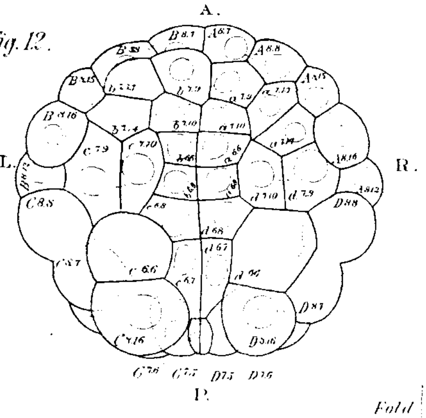

B 8.1
B 8.8
B 7.3
B 8.15
B 7.2
B 8.16
B 7.7
B 8.12
B 7.5
B 8.11
L.
B 7.1
C 7.3
C 7.1
C 8.14
C 8.13
C 8.15
P.

Fig. 12.


A.
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B 8.8
A 8.8
B 8.15
b 7.11
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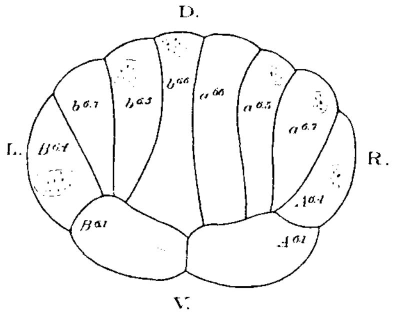
a 7.9
a 7.11
A 8.15
B 8.16
b 7.4
b 7.10
a 7.10
L.
c 7.9
c 7.10
b 66
a 66
a 7.4
A 8.16
R.
B 8.12
b 6.8
a 6.8
d 7.10
d 7.9
A 8.12
C 8.8
c 6.8
D 8.8
d 6.8
d 6.7
C 8.7
c 6.6
c 6.7
d 66
D 8.7
C 8.16
D 8.16
C 7.6
C 7.5
D 7.5
D 7.6
P.

Fig. 15.


D.
b 6.7
b 6.5
b 6.6
a 66
a 6.5
a 6.7
L.
B 6.4
R.
A 6.4
B 6.1
A 6.1
V.

Fold here.

E. Meisel lith. Boston.

IX.

WAVE LENGTHS OF ELECTRICITY ON IRON WIRES.

By Charles E. St. John, A. M.

Presented by Professor John Trowbridge, May 9, 1894.

Since the experimental demonstration of the existence of the oscillating electric discharge, it has been an interesting field of investigation to ascertain whether the magnetization of iron and nickel can follow such rapidly alternating impulses as are obtained by the oscillating discharge of a condenser through a circuit of low self-induction, and, if magnetization does follow, in what way and to what extent can it affect the character of an electric wave propagated along wires of magnetic material.

The results of investigation have shown considerable disagreement, as will be seen from the following brief *résumé* of the investigations bearing upon these points. The questions referred to did not distinctly appear in all the investigations, as they have arisen since; but results were obtained and published which directly relate to at least one of the points under consideration.

M. Savary announced, as early as 1826, that, when a needle was placed in a spiral through which a Leyden jar was discharged, reversals of polarity were obtained by varying the quantity of discharge through the spiral; and Faraday * adduces the magnetizing of needles and bars by common (static) electricity as evidence of its identity with Voltaic electricity, and in his experiment to show that common electricity can deflect the magnetic needle, when a Leyden battery is discharged through the galvanometer, he states the fact that the magnetism of the needle may be removed or reversed by the discharge.

Professor Henry † repeated the experiments of Savary with great skill and care. He obtained reversals of polarity by increasing the quantity of electricity discharged through the spiral in which the needle was placed, while the direction of the discharge remained the same, and by varying the distance between the primary and secondary.

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* Experimental Researches on Electricity. 1833.

† Writings of Joseph Henry, p. 201. 1842.

This anomalous result was referred by Professor Henry to an action of the discharge of a Leyden jar never before recognized. He here first describes the oscillating character of such a discharge as follows: —

"The discharge, whatever may be its nature, is not correctly represented (employing for simplicity the theory of Franklin) by the single transfer of an imponderable fluid from one side of the jar to the other; the phenomena require us to admit the existence of a principal discharge in one direction, and then several reflex actions backward and forward, each more feeble than the preceding, until equilibrium is obtained. All the facts are shown to be in accordance with this hypothesis, and a ready explanation is afforded by it of a number of phenomena which are found in the older works on electricity, but which have until this time remained unexplained."

The apparent change in the direction of the induced currents with a change in distance between the primary and secondary circuit, as indicated by a change in the direction of the magnetization of the needle, was shown to be due to the fact that the discharge of the Leyden jar does not produce an induced current in a single direction, but several successive currents in opposite directions.

There can be no doubt that these discharges were oscillatory in character, and that steel needles and bars were magnetized by them, sometimes by the direct discharge, sometimes by the current induced in a neighboring circuit, sometimes by the first impulse, sometimes by the second or return impulse.

Feddersen * was of the opinion that iron might show some deviation from the behavior of copper and lead; of the last two he says, that the time between two consecutive like-directed current maxima is independent of the cross section and the specific conducting power of the wires forming the circuit, and also of the density of the accumulated electricity. And in regard to iron he adds the following note: "Beim Eisen könnte in Folge der Magnetisirungen eine Abweichung hervortreten: indess zeigt der Versuch dass dieselbe keinenfalls bedeutend ist, übrigens in dem Sinne erfolgen müsste, als wenn die Electricität beim Eisen ein grösseres Hinderniss fände als bei den übrigen Metallen."

The rate of oscillation obtained by Feddersen was one million per second.

The late Professor Hertz † gives in his first paper some experiments that bear upon this subject. He was of the opinion that an

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* Poggendorff, Annalen, CVIII. 499. 1859. † Ibid., XXXI. 429. 1887.

iron wire in an oscillating circuit might be equivalent to a copper wire of greater length, owing to the higher self-induction of iron. He based his opinion upon the known fact that for slowly oscillating currents the self-induction of iron is eight or ten times greater than that of a copper wire of the same dimensions.

He says: "I therefore expected that short iron wires would produce equilibrium with longer copper wires. This expectation was *not confirmed*; the branches remained *in equilibrium* when the copper wire was replaced by an iron wire of equal length. If the theory of the observations here given is correct, this can only mean that the magnetism of iron is quite unable to follow oscillations so rapid as those with which we are here concerned, and that it therefore is without effect." *

The rate of oscillation here used was approximately one hundred million per second, and the diameter of the wires was two millimeters.

In the same paper, he gives another experiment of like tenor. He brought the primary and secondary into resonance, and then in one instance he surrounded one side of the rectangular secondary by an iron tube, and in a second instance he replaced this side by an iron wire of the same diameter as the copper wire. In each case he found the secondary still in resonance with the primary, and was confirmed in his former conclusion. The secondary employed was a rectangle 180 cm. long and 75 cm. wide, and only a length of 75 cm. out of the total length of 510 cm. was changed. The diameter of the wires was 2 mm., and the spark micrometer was used to test for resonance.

In a later paper † on the "Finite Velocity of Electromagnetic Actions," he compares the rate of propagation along copper wires of various diameters, and also the rate of propagation along copper wires with that along iron wires.

He says: "If we replace the copper wire previously used (diam. 1 mm.) by a thicker or a thinner copper wire, or by a wire of another metal, the nodal points are found to remain in the same positions. Thus the rate of propagation in all such wires is the same, and we are justified in speaking of it as a definite velocity. Even iron wires are no exceptions to this general rule; hence the magnetic properties of the iron are not called into play by such rapid disturbances." ‡ (100,000,000 reversals per second.)

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* Electric Waves, p. 36.

† Poggendorff, Annalen, XXXIV. 551. 1888.

‡ Electric Waves, p. 113.

Professor Oliver J. Lodge remarks as follows in his "Modern Views of Electricity" (page 101, 1889): "I might go on and say that iron makes an enormously worse conductor than copper for rapidly alternating currents. So it does for currents that alternate with moderate rapidity — a few hundred or thousand a second — like those from a dynamo or telephone; but, singularly enough, when the rapidity of oscillation is immensely high, as it is in the Leyden jar discharges and lightning, iron is every bit as good as copper, because the currents keep to the extreme outer layer of the conductor, and so practically do not find out what it is made of."

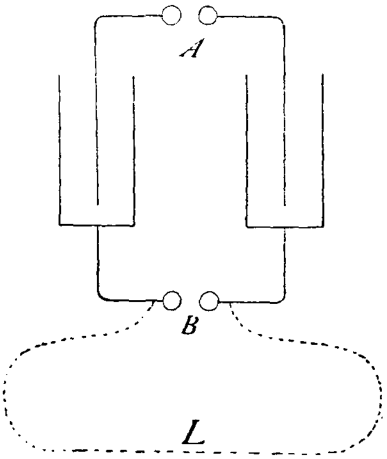

FIG. 1.

And again in more detail on page 46 of his "Lightning Conductors and Lightning Guards" (1892) we find the following: "But every one will say — and I should have said before trying — surely iron has more self-induction than copper. A current going through iron has to magnetize it in concentric cylinders, and this takes time. But experiment declares against this view for the case of Leyden jar discharges. Iron is experimentally better than copper. It would seem, then, that the flash is too quick to magnetize the iron; or else the current confines itself so entirely to the outer skin that there is nothing to magnetize."

The experiment given to substantiate this conclusion is that of the alternate path, as shown in Figure 1. The Leyden jars are charged by an electrical machine, and when a spark occurs at A the charges on the outer coatings may combine by sparking across B or flowing around L. For the path L was used a strip of tinfoil 21 feet long and 3 inches broad, in one case zigzagged backwards and forwards with paraffine paper insulation to abolish self-induction as far as possible, and in the other case wound upon a glass tube to produce as much self-induction as possible.

When the path L was made by the tinfoil zigzag, the critical distance at B, when sparks sometimes passed and sometimes failed for a given spark distance at A, was 0.6. When the zigzag was replaced by the spiral, the critical spark length at B rose to 6.4. A bundle of finely divided iron was now inserted in the spiral, and the critical length continued still to be 6.4.

He remarks on this result as follows: "Here is magnetic time-lag raised to an extreme. . . . It may be said that the iron fails to get magnetized because of the opposing action of the inverse 'Foucault' current induced in it, just half a period behind the inducing currents. I thought this would be so, of course, with thick iron rods, but with a bundle of thin wires I felt doubtful. . . . Whatever the explanation, the fact of time-lag is patent. Yet there is something strange about it, for that a steel knitting-needle can be magnetized by discharging a Leyden jar round it is mentioned in every text-book, and it is certainly true. There are points here requiring further examination." *

So far the investigations that had in view the effect of iron upon extremely rapid rates of oscillation have given but negative results, though both investigators quoted expected to find that the magnetic properties of the iron would be shown under such conditions. Some positive results showing that the magnetic properties of iron still have some effect upon rapid electric discharges have been obtained by the following observers.

Professor John Trowbridge has proved † that the magnetic character of a conductor is by no means unimportant with 1,000,000 double oscillations per second. In brief the experiment and the results were as follows. The oscillating circuit consisted of a Leyden jar and two parallel wires 30 cm. apart and 510 cm. long. These parallel wires could be replaced by others of different diameter and material. A spark micrometer with tin terminals was included in the circuit, and when the discharge occurred the spark was photographed by means of a rapidly revolving mirror.‡

The following results bear upon the subject under investigation. When the parallel wires were of copper (diam. 0.087 cm.), the number of double oscillations on the negative averaged quite uniformly 9 or 9.5; but when an annealed iron wire (0.087 cm. diam.) was substituted, only the first return oscillation was distinctly visible, with sometimes a trace of the first duplicate.

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* Lightning Conductors and Lightning Guards, p. 48.

† Proceedings of the American Academy, XXVI. 115.

‡ Ibid., XXV. 109.

With copper wire (diam. 0.027 cm.) five complete oscillations were quite uniformly visible, but with iron wire (diam. 0.027 cm.) only the first return discharge after the pilot spark was faintly visible.

The time of the double oscillation for the large-sized copper wire was 0.0000020 sec., and for the small copper wire 0.0000021 sec. The author concludes that the magnetic permeability of iron wires exercises an important influence upon the decay of electrical oscillations of high frequency, and that currents of such frequency as occur in Leyden jar discharges magnetize the iron. The data were not sufficient to determine whether there was a change of period, but showed that it must be small if such an effect was produced.

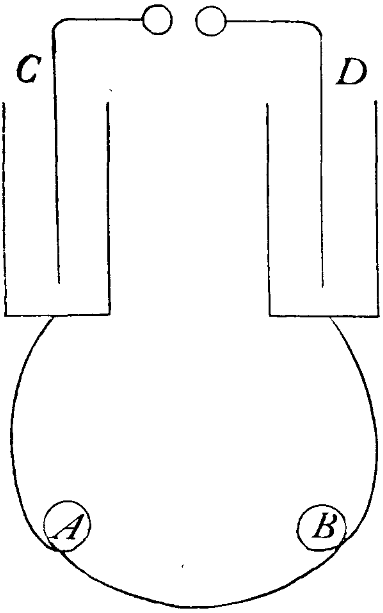

Fig. 2.

Professor J. J. Thompson has stated that the presence of iron can affect the rapidly oscillating electric discharges through a rarefied gas. His method of showing the phenomena is given in Figure 2. C and D are Leyden jars with a spark-gap in the circuit joining their inner coatings, and A and B are two loops in the circuit joining their outer coatings. In the loop A is placed a bulb exhausted to such a degree of sensitiveness that a small change in the electromotive intensity acting upon the bulb produced a considerable effect upon the appearance presented by the discharge. If, when the bulb at A is brilliantly illuminated by the discharge through it, an iron rod be placed in B, the discharge in A ceases; but if a brass rod is placed in B, the discharge in A is unaffected.

The author says: "A striking illustration of the difference between iron and other metals is shown when we take an iron rod and place it in B, the discharge in A immediately stops; if now we slip a brass tube over the iron rod, the discharge in A is at once restored. If, on the other hand, we use a brass rod and an iron tube, when the rod is put in without the tube the discharge is bright. If we slip the iron tube over the rod, the discharge stops." *

In a paper upon the "Absorption Power of Metals for the Energy of Electric Waves," † Bjerknes has given some results which show the great damping power of magnetic metals upon electric oscillations of very high frequency (100,000,000 double oscillations per second). The apparatus used was, in a slightly modified form, the Hertz vibrator and circular resonator, but in place of the spark micrometer in the resonating circuit he used a much more exact and sensitive arrangement, — a kind of quadrant electrometer with two quadrants to which the ends of the resonating circuit were directly joined. He employed among others resonators of copper, iron, and nickel identical in size and construction. The length of wire in each case was 123 cm. and the diameter 0.5 mm. The length of wire joining the plates of the Hertz vibrator could be varied at pleasure. By varying this, the length of wire necessary for best resonance was found in each case, and the electrometer throws were observed for five different lengths of the primary circuit, including the one for best resonance effects. The graphic representation of these results shows plainly that the metals differ greatly in their power of damping electric oscillation. The electrometer throws were much smaller for the iron and nickel than for the copper, and the curves for iron and nickel come less sharply to a maximum. He further conclusively shows that the damping power of the metals experimented upon increases with their resistance and magnetic susceptibility, and concludes that the magnetic properties of iron and nickel are called into play by their extremely rapid alternations of the magnetizing forces. He notes the fact that the maxima for iron and nickel seem somewhat displaced to one side, which may indicate a greater period. but says that such a displacement of the maxima enters in case of greater damping, so that best resonance does not correspond to exactly equal periods of the two circuits, and adds that a quantitative investigation is necessary to determine to which of the two causes the effect may be referred.

From this brief survey of the field, it is seen how, with more exact and refined means of measurement, some of the results expected, when magnetic metals replaced copper in circuits through which rapid electric discharges were taking place, have finally been observed.

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* Phil. Mag. (5.), XXXII. 456. July, 1891.

† Poggendorff, Annalen, XLVII. 69. 1892.

Thompson has shown that iron absorbs more energy than brass when subjected to rapidly alternating magnetizing forces, while Trowbridge and Bjerknes agree in showing that iron and nickle conductors damp out electric waves much more rapidly then copper, and all agree that the magnetic properties of iron are called into play under such conditions.

It has seemed to the writer that it was still an interesting and profitable field to investigate whether the magnetic properties of iron were acted upon sufficiently, and in such a way as to produce a change in self-induction that would affect the rate of propagation of electric waves along iron wires. With this end in view, it was sought to simplify some of the apparatus hitherto employed, and to arrange it so that the effect, if observed, could not be due to any other cause than the magnetic properties of the metals experimented upon.

Description of the Apparatus.

For producing the oscillations, the ordinary Hertz vibrator (Fig. 3) was employed, consisting of two plates of zinc, each 40 cm. square, 61 cm. apart, and mounted upon insulated wooden supports. These supports had square wooden bases that could slide in a grooved plank, so that their distance apart could be easily varied, and by turning the supports through a quarter revolution the plates could be made to face each other or to stand in the same vertical plane. The plates were joined by a conductor of brass 0.5 cm. in diameter, which was connected to the plates by sliding with friction into brass tubes 15 cm. long soldered to the plates. The conducting wire was broken by a spark gap, provided with brass balls 3 cm. in diameter. Tin balls were tried, and had perhaps a little greater effect in exciting oscillations in the secondary; but they required polishing fully as often as the brass balls. Finally brass balls with platinum faces were used, and were found to be much more constant in effect than either brass or tin. A circular piece of platinum 0.025 cm. thick and 2 cm. in diameter was wedged into a shape to fit the front of the ball and there countersunk so that the joint was smooth. At first a piece of platinum 1 cm. in diameter was tried, but this was too small, and frequently the sparks jumped from the edge of the platinum or brass. These were discarded, and the larger platinum faces employed. In a very few minutes after polishing they would often reach a state that would remain constant through a long series of observations, but frequently several trials would have to be made before such a satisfactory condition was obtained. All the observations given below were made with the platinum-faced balls. For polishing the balls a chamois skin with a very small amount of rouge was used, and sometimes they were finally cleansed with alcohol, but this seemed to be no great advantage.

On each side of the spark gap was a hard rubber vertical rod, through which the conducting wire was passed and clamped by a screw. These made a firm support, and held the balls rigorously at the fixed distance apart. The leading wires from the induction coil were soldered to closely fitting short brass tubes that were passed over the conducting wires and rested against the rubber supports. They always remained in the same position, and did not need to be disturbed when the balls were removed for polishing.

A large induction coil (53 cm. long and 19 cm. in diameter) was used to charge the plates of the vibrator. To excite the coil five storage cells were employed, which worked with uniformly good results. The coil was capable of giving a spark 15 cm. long with this source of electromotive force. A sparking distance of 4–6 mm. was found most effective in producing oscillations in the secondary circuit.

The particular feature of the apparatus that applied directly to the investigation was the secondary circuit. In the previous determinations of the wave length due to the Hertzian vibration, the arrangement originated by Hertz and modified by Lecher [*] and by Sarsin and De la Rive [†] has been generally employed. In this arrangement secondary disks were placed face to face with the plates of the vibrator, and to each secondary disk a long wire was attached, and these wires then carried through the air parallel to each other, with sometimes an additional disk on the free ends.

With such an arrangement no exact adjustment of the length of the secondary circuit was required in order to excite vigorous oscillation in it, for the direct electrostatic induction between the plates of the primary and the disks on the ends of the secondary wires was so great that powerful oscillations were produced along the secondary wires, whatever their length might be, and several systems of waves could be detected which seemed to give experimental grounds for believing that the wave system sent out from the Hertzian vibrator was very complex.

The capacity of the vibrator is increased by the presence of these secondary disks so near to the plates of the vibrator, so that the wave length found under these conditions is not due to the simple Hertzian vibrator, but to a very heavy complex oscillating system with somewhat obscure internal reactions. Lecher calls attention to the change in the sound of the spark when the two parallel wires of the secondary circuit are bridged across by a conductor, and there is a very marked difference in the spark when the secondary circuit is removed entirely, the spark losing much in body and explosive character. The secondary under these circumstances must exert a strong reaction upon the primary.

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[*] Poggendorff, Annalen, XLI. 850

[†] Archives des Sciences Physiques, XXIII. 113. 1890.

It seemed desirable to devise some arrangement depending more directly upon the principle of electrical resonance, and one whose use would not increase the capacity of the vibrator and whose reaction upon the vibrator would be a minimum. This was accomplished by omitting the secondary disks and using simply one wire, as shown in Figure 3.

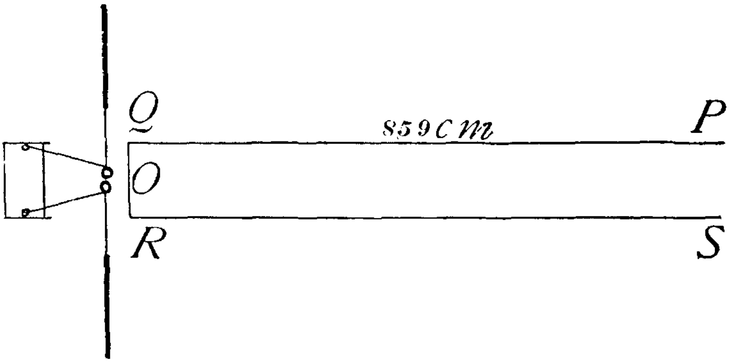

Fig 3.

The secondary circuit consisted of the long rectangle P Q R S, which was carefully adjusted to resonance by placing the exploring terminals of the bolometer (described later) at P S, and then cutting off the ends of the wire until the length was found that would give the maximum effect. Such a maximum was found when P Q was 859 cm. long. The maximum was sharp and unmistakable, the effect falling off rapidly when the wire was either lengthened or shortened. The result is shown graphically in Figure 4, where, as in all the curves given, distances from Q are used as abscissas and deflections of the galvanometer as ordinates.

To determine the character of the vibration along the wire, the lengths P Q and R S were fixed at 859 cm., the exploring terminals were moved along the rectangle, and the bolometer reading taken for each position of the exploring terminals. The graphic representation of the results is shown in Figure 1 of the Plate. The character of the curve indicates a simple form of vibration. The total length of the wire is equivalent to seven half wave lengths. The minimum points are very nearly the same distance apart, and the distance from the minimum occurring at 748 cm. to the centre of the side Q R may be taken as three half wave lengths. This furnishes a ready means of calculating the half wave length: —

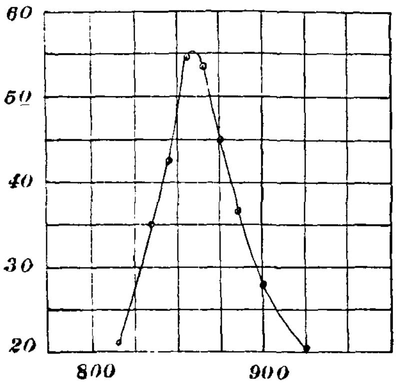

FIG. 4.

$$Q\,R = 30 \text{ cm.} \qquad 748 \times 15 = 763 \text{ cm.}$$

$$763 \div 3 = 254.3 \text{ cm.} = \text{a half wave length.}$$

The distance from this minimum to the end of the wire at P should be one fourth wave length, or 127.15 cm. The actual distance is 859 — 748 = 111 cm., so that the correction due to the free end of the wire is about 16 cm.

To adjust the length of the wire under this arrangement was a work of considerable difficulty; for in finding the points of maximum effect many trials had to be made, and the wire cut off a few centimeters at a time and then renewed many times. To remove this source of inconvenience, the ends P and S were wound on wooden bobbins, so that shortening and lengthening could be produced without cutting the wire. This was a marked improvement, but the changing size of the coils, as the wire was shortened or lengthened, varied the capacity at the end slightly, and somewhat irregularly. This led to the adoption of the arrangement shown in Figure 5.

The secondary circuit consisted of the rectangle K L M N. The side L N was open, and the lengths of the sides K L and M N could be varied between a few centimeters and ten meters. The ends of the wires K L and M N were in reality formed by the small copper

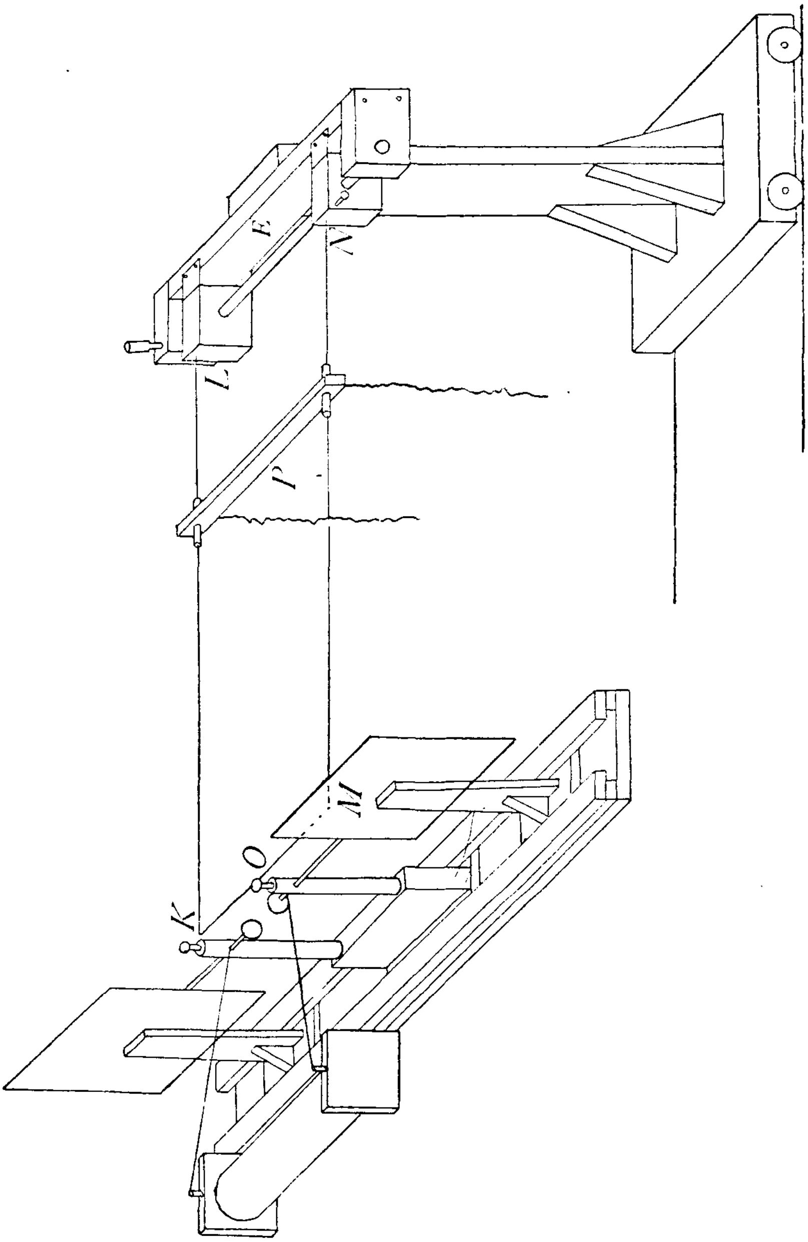

Fig. 5.

boxes L and N. These were 10 cm. square and 4 cm. thick, and mounted upon the wooden bar E by insulating supports. Within the boxes were wooden bobbins fixed to a hard rubber axle, and each capable of holding 10 m. of the largest wire experimented upon. In the front of each box was a small opening for the passage of the wire, but, to assure a firmer contact between the wires and the boxes, a brass block was soldered on the inner side of the front and a binding screw passed in from the outer side of the box. The bar E was fastened to a wooden support resting upon the car, which ran on a wooden track extending the entire length of the room. The car carried a brake, so that the wires could be drawn taut, and the wooden screw held the axle from turning. With this arrangement the length of the wires could be varied at will, while the end capacities would remain constant. The end capacities are not a feature desirable for their own sake, as they destroy the perfect simplicity of the plain rectangle and seem to detract somewhat from the sharpness of the maximum; but the gain in convenience, and the possibility of obtaining a large number of observations whose average values can be used, quite overbalance these considerations in most cases where the apparatus may be applied.

In the early part of the investigation the "Foucault" interruptor was used, but it was extremely irregular in its action, and caused endless annoyance. It ran at an ever varying rate, and required repeated adjustment and constant attention. To remedy at least some of these defects, an interrupter actuated by a small electric motor was devised.* The results obtained from this motor-interruptor were so satisfactory that a detailed description is added.

A Porter's motor, No. 1 (Fig. 6, M), was used to produce the motion. This was actuated by the current from two storage cells, and it ran at a fairly constant speed. The armature of the motor was wound in three sections, and was thus free from dead points, giving it the great advantage for the present purpose that it could be set in motion simply by closing the circuit, making it possible to control it from the observer's station. The motor was geared to the two-crank shaft K by means of a wheel and pinion. The wheel and pinion had the ratio of 144 to 24 in the following investigation, but the motor could slide on the brass bed-plate so that pinions of other sizes were available. The speed of the shaft K was about 750 revolutions per minute, and about 25 breaks were produced per second. The plunging rods were thinned down at O so that they were flexible and gave the required freedom of motion; they ran through the bed-plate and the brass bar below, which served as guides. The plunging rods carried lock-nuts by which the flexible coils leading the current from the brass post Q were attached. The lower ends of the plungers were of platinum wire, No. 18. The glass mercury cups had brass bottoms that screwed into the brass arm N, which was adjustable by means of the collar and binding screw L along the pillar P. At P was attached one pole of the battery actuating the coil, and also one pole of the condenser in the base of the coil, and at Q was attached one pole of the coil and the other pole of the condenser.

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* This and the other apparatus especially prepared for this investigation, and requiring much technical skill in its construction, was made by the mechanician of the laboratory.

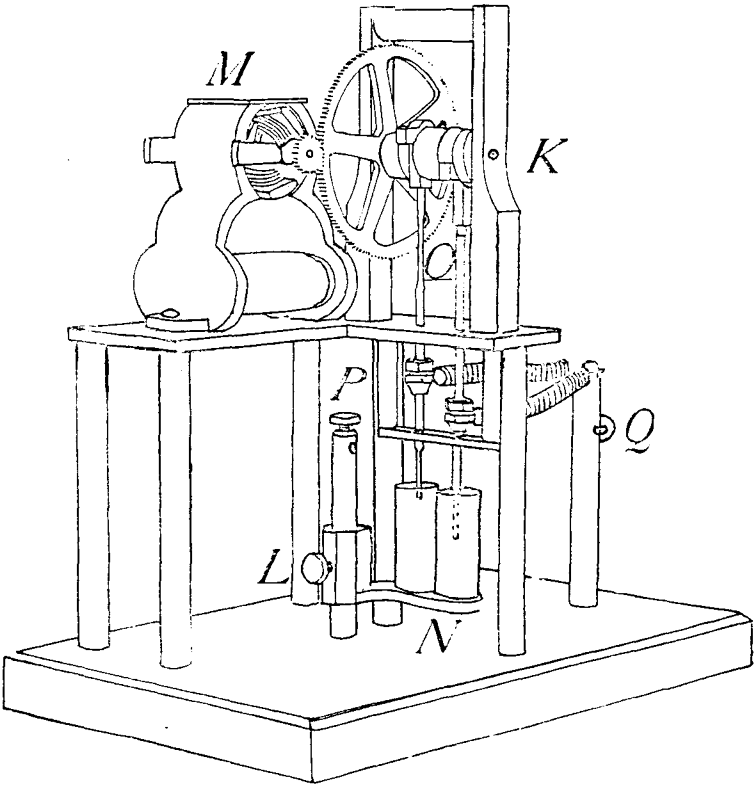

Fig. 6.

The cups were filled with mercury to a height of about 8 mm., and then filled with alcohol to within a few millimeters of the top. They usually required cleaning only after several hours' use, when the surface of the mercury consisted of very fine globules, and sharp breaks of the circuit were not made at each stroke of the plunger, as was indicated by the occasional failure of the spark. The length of the spark was kept constant during the observation, and the character of the spark depended much upon the exact adjustment of the height of the mercury cups of the interruptor. While it and the coil were both in action, the height of the cups was adjusted until the sparks came regularly with a peculiar crashing snap, and showed the bluish white thick body that Professor Hertz described. Both the ear and eye were soon so trained that they gave quick and sure information of the character of the spark, but the ear was better than the eye. The exact height of the mercury cups was of the utmost importance, a slight difference in height changing the character of the spark greatly. The exact point was best found by concentrating the attention upon the sound, and then slowly raising or lowering the cups, when suddenly there would seem to be a rhythm between the sound of the interruptor and the snap of the spark, which would disappear with further motion up or down. This rhythm would indicate that for every break of contact there was a corresponding pilot spark between the micrometer balls.

For measuring the effects produced in the secondary circuit, the bolometer as designed by Paalzon and Rubens * was used with most satisfactory results. The bolometer was constructed according to the description given by them in the paper referred to, and differed only in minor details arising from the circumstances and the materials obtainable. The accompanying diagram is theirs, but the following description applies in all its details only to the instrument constructed for this investigation.

The bolometer is in reality a double Wheatstone bridge. The four arms of the bridge are the resistances W_1, W_2, W_3, W_4, of which W_1 and W_2 are quadrilateral circuits of equal resistance, and W_3 and W_4 are coils of equal resistance. The quadrilateral A B C D, or W_2, is really a small Wheatstone arrangement, used as one branch of the main bridge. For convenience in description, W_2 will be called the "bolometer branch," and the term bridge limited to the Wheatstone

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* Anwendung des bolometrischen Princips auf electrische Messungen. Poggendorff, Annalen, XXXVII. 529.

net, of which W_2 is a portion. If in the quadrilateral A B C D the sides are of equal resistance, and if then a current be led in at B and out at D, or *vice versa,* no difference of potential will be produced between A and C; in the same way, a current can be led in at A and out at C without producing any potential difference between B and D. The two currents can traverse the rectangle simultaneously and exert no effect upon each other arising from difference of potential. If, after the bolometer branch and the bridge are both balanced, a current, alternating or direct, is sent through the bolometer branch W_2 from B to D, none of the current will pass through the galvanometer; but the resistance of the branch W_2 will be increased by the evolution of heat, and the bridge thrown out of balance, as indicated by the deflection of the galvanometer.

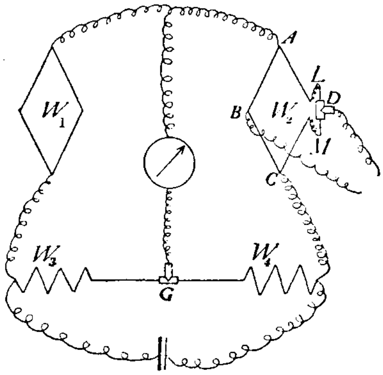

FIG. 7.

The resistances W_3 and W_4 were coils of fine German silver wire double wound on wooden spools, and of three ohms' resistance each. The quadrilaterals W_1 and W_2 were of iron wire, radius 0.035 mm., and each side had a resistance of three ohms. The arms of the bolometer branch W_2 were balanced before use by means of the sliding mercury contact D, so that no deflection was produced in the galvanometer when a steady current was passed from B to D. The sliding mercury contact consisted of 20 cm. of No. 18 German silver wire, L M, and a sliding block of brass, D, which contained in its upper surface a small cup-shaped cavity filled rounding full with mercury. The German silver wire was amalgamated to insure a good contact. The contact G was of similar construction. The connections were of No. 18 copper wire, whose resistance was negligible in comparison with the bridge arms.

The adjustment of the bolometer branch, once made, remained constant through the series of observations, but the bridge adjustment by means of the sliding contact G had to be made frequently. To supply the bridge current a Daniell cell was used with a resistance of 5 to 30 ohms in circuit.

The galvanometer was of the Thompson type and had a resistance of 56.9 ohms, and a figure of merit of 2.3×410^{-8}, with a scale distance of 1 m. and scale divisions of 1 mm. The time of a half vibration of the needle was 7 seconds.

The bolometer resistances were attached to the under side of the cover of a well made box of cherry (33 cm. long, 26 cm. wide, and 8 cm. deep). The resistances W_1 and W_2 were supported on slender posts, so that they came nearly in the middle of the box, and were equally exposed to the air on all sides. On the upper side of the cover were the binding posts and sliding contacts. This box was placed inside another one of similar construction (47 cm. long, 39 cm. wide, and 23 cm. deep), and the space between was packed with cotton wool. Cords from the sliding contacts were led through the sides of the outer box, so that adjustments of the arms could be made without exposing or touching the bolometer. Even with this protection from thermal changes, much difficulty was experienced when the hot weather came, and the temperature of the room could not be kept constant. It was found, however, that early in the morning very little disturbance was experienced, and most of the observations whose results are reported were recorded before the heat of the morning was much felt in the room containing the bolometer.

To use the bolometer for measuring the energy at all places on the wires forming the secondary circuit, the arrangement devised by Rubens * was used. Over the two wires K L and M N (Fig. 5), were slipped thick-walled capillary tubes of glass, about 5 cm. long, and these were held by a small wooden bar, so that they could be slipped along together. This arrangement is spoken of hereafter as the exploring terminals. The ends of the lead-wires to the bolometer were wound once around the tubes and fastened by sealing wax. These formed two Leyden jars of extremely small capacity, and the oscillations of charge on their inner coatings, which were formed by the wires K L and M N, produced rapidly oscillating currents through the bolometer resistance W_2. For leading wires to the bolometer silk covered copper wire No. 36 was used that had been drawn through hot paraffine. Larger wires were tried and wires with rubber insulation, but with these the apparatus was less sensitive.

The following method was pursued in taking the observations. The interruptor was set in action, the circuit closed through the induction coil, and an observation taken of the first swing of the

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* Ueber stehende electrische Wellen in Drähten und deren Messungen. Poggendorff, Annalen, XLII. 154

needle. The circuits were broken as soon as the needle reached the end of its first swing, and the extent of this excursion was the reading recorded. In accordance with the experience of Paalzow and Rubens, it was found that a steady deflection could not be obtained, but this first swing was, under like conditions, quite constant, and a preliminary calibration of the instrument by passing currents of known strength through the bolometer branch W_2 showed that the square root of the deflection was in a constant ratio to the current. The needle was quickly damped by making and breaking the circuit through the induction coil, with the interruptor in action.

The rooms at disposal were very suitable for such an investigation. The main room was 18 m. long, 6 m. wide, and 5.5 m. high, and it contained a very small amount of metal, and as it was in the non-magnetic part of the laboratory that small amount was of brass and bronze except the temporary addition of a small steam radiator in the corner back of the oscillator. The oscillator was placed at 4.5 m. from one end, and the parallel wires ran through the middle of the room at a distance of 1.6 m. from the floor. The leading wires carrying the currents from the batteries were of twisted cable and placed high up against the walls. The bolometer and galvanometer were in an adjoining room, where the observation table was equipped with the keys necessary for complete control of the interruptor and induction coil. By this means it was possible for one person to carry on the investigation, though it was very trying. Not only were the observer's eyes in use, but it was necessary to listen intently to the sparking of the oscillator, as after some experience very slight changes could be detected and a close judgment formed of the steadiness of the spark; besides, it was necessary to note the sound made by the interruptor, as small variations in its speed were easily noticed. The only time the interruptor was likely to show much change in speed was when the battery was beginning to fail, or the brushes had become worn.

The theory of the investigation was based upon the principle of electrical resonance.

Bjerknes has shown, in the paper previously noted, that, if damped electromotive impulses obeying a sine law be assumed to act upon a secondary circuit, there will be produced in the secondary circuit oscillations of the period belonging to the primary impulses, and at the same time oscillations proper to the secondary circuit, and that these induced oscillations will reach their maximum amplitude when the two circuits have the same period. His investigations also show that the oscillations of the Hertz vibrator damp out much more rapidly than the oscillations in the secondary, at least when there is no spark gap in the secondary circuit.

The sides of the rectangle (Figure 5) were reduced to a few centimeters in length, so that it could be safely assumed that its period was much shorter than that of the vibrator. The plates of the vibrator were fixed at 61 cm. apart, and the side K M of the rectangular secondary was placed at 6 cm. from the conductor joining the plates of the vibrator, with its centre O opposite the spark gap. The sides K L and M N lay in the horizontal plane through the axis of the vibrator, and were held by the end supports at 30 cm. apart. The apparatus was symmetrical about a vertical plane through its spark gap normal to the axis. The exploring terminals were kept at L N and bolometer readings taken for each small addition to the length of the sides K L and M N. When best resonance was obtained with the shortest length of the secondary circuit that gave a maximum, it was assumed that the secondary had the same period as the primary, and that its equivalent length was a half wave length, its actual length depending upon the effect due to the free ends. The occurrence of resonance is a very marked phenomenon, even with a vibrator that damps as rapidly as the Hertzian. The following table shows two series of readings for the first maximum when an iron wire was used:—

Length of side of rectangle	15	25	35	40.0	42.5	45.0	50	60	75
Deflections	107	145	156	194.3	199.2	181.5	140	81	42
Deflections	94	119	161	185.0	191.0	178.0	136	76	34

There can be no free motion of the electricity at the ends of the secondary circuit, but an accumulation alternately positive and negative and the resulting alternation of potential, the phase at L being always opposite to the phase at N. Elsewhere along the circuit the electricity moves with more freedom and less accumulation. The point O may be called the electrical middle of the circuit, where the accumulation is least and the movement most restrained. The electromotive impulses from the vibrator act directly upon the side K M. so that O remains a point of free motion, or the central segment of the wave, while L and N are always places of no electric motion, or the nodal points. The nodes under this view are the places of greatest potential difference, so that in the graphic representation of the results the maximum points of the curves correspond to the nodes, the bolometer throws being the largest when the exploring terminals are placed where the potential difference is greatest. The shortest circuit being a half wave length long, a second resonating circuit ought to be found by increasing each side of the rectangle by a half wave length, making the circuit 3 half wave lengths long, and a third when the circuit is 5 half wave lengths long, and so on.* This is evident from a consideration of the accompanying diagram. O is the center of a central segment and the points marked 1, 3, 5, are always nodes.

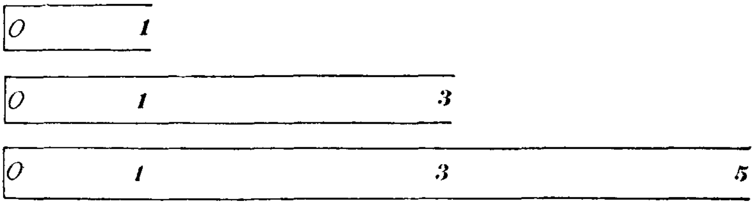

FIG. 8.

From the results that he obtained, Bjerknes concluded that the change of period, if there was such a change, by the use of iron in place of copper, could not exceed two per cent.

The difference in length between a copper and an iron circuit of the same period would be very small with circuits a half wave length long, but this difference would be three times as great with circuits 3 half wave lengths long, and there might be a cumulative difference that would finally become measurable by the use of circuits of still greater length. This theory was tested in the following way. A copper wire (diameter 0.1201 cm.) was used as the secondary circuit in Figure 5. The sides were taken 15 cm. long, and then gradually lengthened to 875 cm., and bolometer readings observed for each addition. The results are shown graphically by the upper curve in Figure 4 of the Plate. The critical points in the curve are the results of many separate determinations. The unsteadiness of the spark in the vibrator made the determinations somewhat laborious, though a single series of observations would locate a maximum very closely. After this had been done, a space of about a meter including the maximum point was worked over forward and back, changing its length 2.5 to 5 centimeters at a time in the region of the maximum. To assure the steadiness of the spark during such a series of observations, some convenient length of circuit was chosen as a point of reference, and observations taken before and after the series; if these showed that the activity of the spark was practically the same, the readings of the

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* J. J. Thompson, Recent Researches in Electricity and Magnetism, § 297.

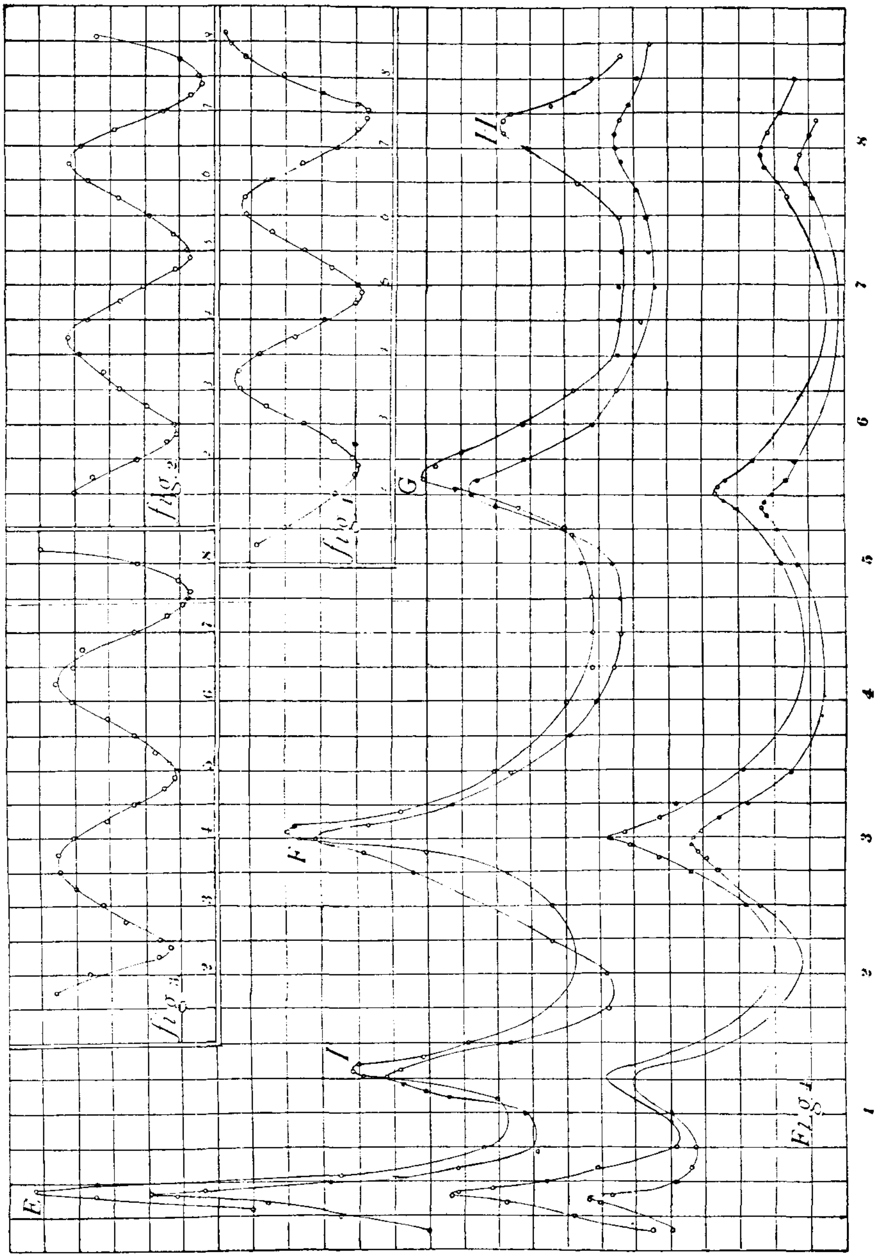
fig. 2
fig. 3
fig. 1
Fig. 4
E
F
G
H
I
1
2
3
4
5
6
7
8

series were retained. The results here given rest upon such readings.

An examination of the curve shows four maxima, E, F, G, H, occurring when the sides of the rectangle were 45, 306, 562.5, and 818 cm. long. The additions of wire for the successive maxima after the first were 261, 256.5, and 255.5 cm. These additions should be a half wave length; the last two are nearly the same, but the first differs by 5 cm. from the average of the last two, which is 256 cm. With the sides fixed 818 cm. long, the wave form along the circuit was determined by sliding the exploring terminals over the wires by short steps, and observing the bolometer throws for each position. The result is shown in Figure 3 of the Plate. The critical points were determined several times, and a method similar to that described above was used to assure the constant activity of the spark. The curve shows three minima, occurring at 240, 496, and 752 cm. Starting from the point O these give half wave lengths of 255, 256, and 256 cm., with an average of 255.6 cm. The third minimum at 752 was determined with care, as it was to be used as a basis for calculating the half wave length. A small error in determining the position of this miniumm would be divided by 3 in obtaining the result, since its distance from O was 3 half wave lengths. The total length of the circuit was 7 half wave lengths. From the third minimum to the end it was one fourth of a wave length, the capacities bring each equivalent to 62 cm. of the wire. By fixing the length of the rectangle at 562.5 and 306, a similar investigation showed the circuits to be respectively 5 and 3 half wave lengths long.

An explanation of the fact mentioned above, that the distance between the first and second maxima was anomalously large, may possibly be this: the sides of the rectangle for the first maximum were but 45 cm. long, so that the effect of the closed end in increasing the self-induction was relatively large, and the maximum appeared earlier than it otherwise would; but when the rectangle was 300 cm. long, the influence of the closed end became relatively small, and the second and future maxima came in the normal positions. In the first case the capacity was mostly local, while in the second it was largely distributed, and the length of the circuit was greater than the wave length. This same effect appeared in every case, and seemed to be a constant phenomenon.

The maximum I, omitted from the above discussion, was not constantly present, but appeared when the primary spark was particularly active, and seemed to belong to a circuit whose period was to the period of the primary as 5 to 3. The side of the rectangle was 127.5 cm., and the end capacities equivalent to 62 cm. of wire. The half wave length was

$$30 + 127.5 \times 2 + 62 \times 2 = 409. \quad 409 \div 255.6 = 1.6, \text{ nearly.}$$

This was the only indication observed of complexity in the vibration of the oscillator. It appears that, when the oscillator is especially active, it can excite a circuit having this ratio to itself, or that the vibration is not a simple one. Time was not at disposal sufficient to decide this point, which is left for future investigation.

A comparison of the curve (Fig. 1 of Plate) obtained from the plain wire circuit with the curve (Fig. 3 of Plate) obtained when capacities were fixed on the free ends shows a quite satisfactory agreement in the results, which tends to create confidence in both methods. The half wave length by the first is 254.3 cm., by the second it is 255.6 cm., values which differ by about one half of one per cent. There is a marked difference, as was to be expected, in the form of the curve for the quarter wave length next the free ends. When end capacities were used. the accumulation of charge seemed mainly confined to those out of reach of the exploring terminals, while with the plain wire it seemed distributed over a greater distance, and could be detected by the exploring terminals. In each case the effect of the ends was to make the curve depart from its normal form along the free wire.

An annealed iron wire (diameter 0.1186 cm.) was put in place of the copper. and the same series of observations was made as with the copper. The results are shown graphically in the lower curve of the upper pair in Figure 4 of the Plate. The maxima E, F, G, H, appear at 42.5, 301. 553, and 805 cm.; in each case before the corresponding maxima with the copper, and the difference increases with the length of the circuits. as is evident from an examination of the curves. The successive additions after the first maxima are 258.5, 252, and 252 cm.; the last two agreeing, while the first, as with the copper, is larger. With the sides of the rectangle fixed at 805 cm., the form of the wave was found as shown in Figure 2 of the Plate. The third minimum occurs at 740 cm. Calculating its half wave length as before, 740 + 15 = 755. 755 ÷ 3 = 251.6 cm. This agrees well with the value 252 cm. given above by the last two additions, but differs by 4 cm. from the value found when the copper was used.

The same series of observations was repeated with a second pair of finer wires (diameter of copper wire 0.07836 cm., diameter of iron

0.07850 cm.). The results are shown in the lower pair of curves in Figure 4 of the Plate, the upper one, as before, being the copper. A comparison of the curves shows the same general result, which appears more distinctly from the following table.

	1st Maximum.			2d Maximum.			3d Maximum.			4th Maximum.		
	Cu	Fe	Difference.	Cu	Fe	Difference	Cu	Fe	Difference.	Cu	Fe	Difference.
Upper pair	45	42.5	2.5	306	301	5	562.5	553	9.5	818	805	13
Lower pair	40	57.5	2.5	300	294	6	552	540	12.0	799	784	15

The successive differences should be in the ratio of 1, 3, 5, 7, if the theory of the investigation is correct. The differences for the first two maxima are very small, so that the experimental error in their determination would be relatively large.

In the case of the fourth maximum, the damping was so great that it was difficult to fix the point with certainty. The difference for the third maximum was relatively large, and the determination of the maximum point was sharp. Taking this difference as a point of reference, the calculated and observed values are shown in the following table.

	1st Maximum.		2d Maximum.		3d Maximum.		4th Maximum.	
	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed	Calculated.	Observed
Upper pair	1.9	2.5	5.7	5	9.5	9.5	13.3	13
Lower pair	2.4	2.5	7.2	6	12.0	12.0	16.8	15

The observed half wave lengths for the four wires were as follows: —

$\begin{cases} \text{Copper (diameter 0.1201 cm.), 255.6 cm.} \\ \text{Iron (diameter 0.1126 cm.), 251.6 cm.} \end{cases}$

$\begin{cases} \text{Copper (diameter 0.07836 cm.), 251.6 cm.} \\ \text{Iron (diameter 0.07850 cm.), 246.8 cm.} \end{cases}$

The wires in each pair were as near the same diameter as could be found, the iron of the larger pair having slightly the smaller diameter, but the copper being the smaller one in the second case. In other respects the circuits compared were as nearly identical as possible. The capacity per unit length being the same for wires of the same diameter, the shortening of the wave length when iron displaced copper of the same diameter must be caused by an increase in self-induction due to the magnetic properties of the iron. If this is true, it means that the magnetization of iron can be produced and reversed 115 million times per second. This reduces the "time-lag" of magnetization to a very small quantity, if magnetizing forces of such duration are capable of bringing the magnetic properties of the iron into play.

In the case of extremely rapid oscillations, Prof. J. J. Thompson has shown (Recent Researches in Electricity and Magnetism, § 295) that approximately $y^2 = \frac{2}{L' \, C}$, where $\frac{y^2}{4\pi^2}$ is the square of the frequency, and L' is the self-induction for any rapid oscillations, and C the capacity of the system. It is easy from this to calculate an approximate value for the ratio between the self-induction per unit length of the iron and the copper.

Let L = the self-induction of the copper per unit length.
Let L' = the self-induction of the iron per unit length.
Let C = the capacity of either per unit length.

Using as a basis of calculation the data from the third maximum G of the curves of Figure 4 of the Plate, the total length of the copper circuit (diameter 0.1201 cm.) is: —

The sides,	562.5 × 2 =	1125 cm.
The closed end,	=	30 cm.
The equivalent of the end capacities.	62 × 2 =	124 cm.
		1279 cm.

For the iron (diameter 0.1186 cm.) the length is: —

The sides,	553 × 2 =	1106 cm.
The closed end,	=	30 cm.
The equivalent of the end capacities,	61 × 2 =	122 cm.
		1258 cm.

Since the two circuits have the same frequency, the products of the self-induction by the capacity are equal.

$$1258^2 \, L' \, C = 1279^2 \, L \, C.$$

$$\frac{L'}{L} = 1.034.$$

In the same way, for

$$\left\{\begin{array}{l}\text{Copper (diameter 0.0884 cm.)}\\ \text{Iron (diameter 0.08847 cm.)}\end{array}\right. \qquad \frac{L'}{L} = 1.041.$$

$$\left\{\begin{array}{l}\text{Copper (diameter 0.07836 cm.)}\\ \text{Iron (diameter 0.07850 cm.)}\end{array}\right. \qquad \frac{L'}{L} = 1.043.$$

By the use of Lord Rayleigh's formula for induction under very rapid oscillations, it is easy to calculate the permeability of the iron, since the ratio between the self-induction of the iron and copper are given by the previous calculation.

Lord Rayleigh's formula is

$$L' = l\left(A + \sqrt{\frac{\mu R}{2 p l}}\right),$$

where l is the total length of the circuit; A, a constant depending only on the form of the circuit, or $l A$ is the self-induction of a similar copper circuit; μ, the permeability; R, the resistance; $p = 2\pi n$, where n is the number of complete oscillations per second.

The value of $p = 2\pi n = 360,000,000$.

R for iron wire diameter 0.1186 cm. = .1328 ohms per sec.
" " " 0.08847 cm. = .227 " "
" " " 0.0785 cm. = .301 " "

For iron diameter 0.1186 cm.

$$L' = 1.034\, L = l\left(A + \sqrt{\frac{\mu R}{2 p l}}\right),$$

$$L + .034\, L = L + l\sqrt{\frac{\mu R}{2 p l}},$$

$$.034\, L = l\sqrt{\frac{\mu R}{2 p l}}.$$

Calculating the value of L for a copper circuit l units long, substituting the value in the above equation, and solving, we find: —

For the iron wire diameter 0.1186 cm. $\mu = 430$
" " " 0.08847 cm. $\mu = 389$
" " " 0.0785 cm. $\mu = 336$

These values for the permeability all fall within a reasonable limit, and have for an average $\mu = 385$. These are the values found for different specimens of wire made by the same company, but the specimens were wound and unwound and stretched many times during the series of observations.

Besides the shortening of the wave length due to the increased self-induction of the iron, there is shown a decided increase in the damping, as has already been observed by Trowbridge and Bjerknes. In Figure 4 of the Plate the curves for iron fall below the corresponding ones for copper, but owing to the change in the activity of the primary spark no exact measurement was made. It was only observed that the bolometer throws with the copper circuit were always greater than those with the iron circuit of same dimensions when the spark was constant as far as the eye and ear could judge.

A value for the damping factor $\epsilon^{-\frac{Rt}{2L}}$ can be calculated for the iron and the copper. Lord Rayleigh's formula for the resistance under very rapid oscillations is:

$$R' = \sqrt{\tfrac{1}{2} p\, l\, \mu\, R}.$$

For iron wire circuit (diameter 0.1186 cm.),

$$l = 1258\,; \;\; \mu = 430\,; \;\; R = 1.67 \times 10^9\,; \;\; p = 36 \times 10^7;$$

whence

$$R' = 403 \times 10^9\,; \;\; L' = 34 \times 10^3.$$

The damping factor becomes $\epsilon^{-6 \times 10^6 t}$.

The time required for the amplitude to fall to one half of its maximum value is found from the equation $\frac{1}{2} = \epsilon^{-6 \times 10^6 t}$:

$$t = .000000115 \text{ sec.}$$

On the basis of 115,000,000 alternations per second, the number of complete oscillations in this time is 6.5. A similar calculation for the corresponding copper circuit gives nearly sixty times as many.

It has been suggested that the greater damping of the iron might give an apparent change of wave length. If the iron circuit is chosen too short, and the maximum point is sought by adding to the length of the wire, the increase of length would increase the damping and tend to diminish the bolometer throws while the approach to the point of resonance would tend to increase the effect on the bolometer; the two in fact would work against each other. If, on the other hand, the circuit be chosen too long, and resonance is sought by shortening the wire, the two would work together.

If the damping plays an important part we might expect different results under these conditions. Iron wire (diam. 0.08847 cm.) was used, and the circuit shortened until the sides were 15 cm. long and the first maximum point was found by gradually lengthening the wire; it was then found by gradually shortening the wire from an initial length of 60 cm. for the sides of the rectangle. The results are shown in Figure 9 where the upper curve is based on the data found when shortening the wire, and the lower on the data found when lengthening it. The two differ by less than a centimeter, which is as near as two determinations could be expected to agree. In all determinations of the critical points of the curves shown, readings were taken both forward and back, and the averages used as data for the curves.

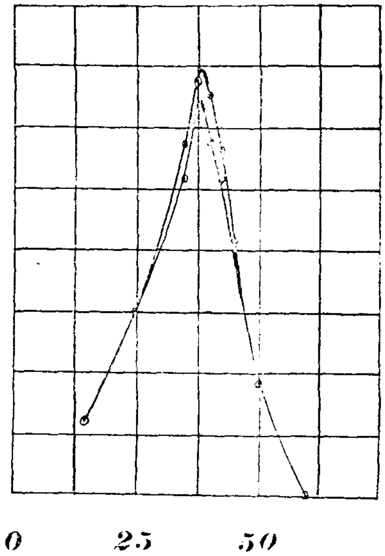

Fig. 9.

Another result of the investigation is apparent when copper circuits are compared in which wires of different diameters are used.

		3d Max G
Copper wire, diameter	0.12010 cm.	562.5
" " "	0.08840 cm.	553.5
" " "	0.07836 cm.	552.0
" " "	0.03915 cm.	535.0

The half wave lengths calculated from this maximum are:—

Copper (.01201 cm.)	255.8 cm.
" (.08840 cm.)	252.2 cm.
" (.07836 cm.)	251.6 cm.
" (.03915 cm.)	244.8 cm.

These are found by taking the total length of the circuit, and dividing by 5.

535 × 2 = 1070 cm., length of wires.
30 cm., length of closed end.
62 × 2 = 124 cm., equivalent of end capacities.
1224 cm.
1224 ÷ 5 = 244.8 cm.

The results here presented differ from those hitherto given, and particularly from those of the late Professor Hertz; but his investigations were made with the spark micrometer as a measuring instrument, and the same is true of Dr. Lodge's work with the alternate path. The adaptation of the bolometer principle to this purpose furnishes a much more accurate means of determining wave lengths and the occurrence of resonance. It is not surprising that a change of wave length of less than two per cent escaped detection by the spark micrometer method. The difference between copper and iron increases as the diameter of the wires diminishes; with wires 2 mm. in diameter, the size mostly used by Hertz, the difference would be exceedingly small.

The range of wires suitable for the study of the phenomena is rather limited. If the wires are larger than 1 mm. in diameter, the difference between iron and copper is slight; while with wires less than 0.5 mm. in diameter the damping is so great that long wires cannot be used and advantage cannot be taken of the cumulative effect which is the basis of the present method. There is no disagreement between the results here given and those reported by Trowbridge and Bjerknes. The circuits Trowbridge used were so long that the iron damped the oscillation too rapidly, and the circuits used by Bjerknes were so short that the difference between the copper and iron could not be determined with certainty.

I wish to express my great obligation to Professor John Trowbridge for the encouragement and suggestions that I have received from him, and for his kindness in placing the resources of the Jefferson Physical Laboratory so completely at my disposal.

CONCLUSIONS.

1. The self-induction of iron circuits is greater than that of similar copper circuits under very rapid electric oscillations (115,000,000 reversals per second). This change in self-induction varies from 3.4 to 4.3 per cent in the present investigation, and increases with decreasing diameters.

2. The increase in self-induction produces greater damping, and a shortening of the wave length of between 1.5 and 2 per cent.

3. The permeability μ of annealed iron wires under this rate of alternation is about 385.

4. For oscillations of the same period, the wave length along parallel copper wires varies directly with the diameter of the wires. Range of wires used 0.03915 cm. to 0.1201 cm. The maximum decrease observed is 5 per cent.

Jefferson Physical Laboratory,
July 24, 1894.

X.

A HEAT METHOD FOR MEASURING THE COEFFICIENT OF SELF-INDUCTION.

By P. G. Spalding and H. B. Shaw.

Presented by Professor John Trowbridge, May 9, 1894.

The coefficient of self-induction of a coil having an iron core and traversed by an alternating current depends upon the permeability of the iron, and therefore upon the current strength, in a manner which can be seen by examining the hysteresis curves of Ewing and others.

If the coil has no iron core, its coefficient of self-induction is constant for all current strengths, and may be measured by some method where the current used is small, "Rayleigh's bridge method," for instance.

If we try to calculate the coefficient of self-induction when a coil with an iron core is subjected to an alternating current, we have a practically impossible problem; but if we regard the effects as a whole, we can measure the *effective* coefficient of self-induction for any given impressed electromotive force.

The effective coefficient of self-induction of a coil having an iron core may be defined as the equal of the constant coefficient of that coil which would give the same integral current flow as the former under the given conditions.

Let us first examine the case theoretically. Given a simple branched circuit and an impressed electromotive force which varies as the ordinate of a sine curve, we obtain the following for the values of the currents in the two branches: —

$$(1) \qquad i_1 = \frac{I\sqrt{R_2^2 + p^2 L_2^2}}{\sqrt{(R_1 + R_2)^2 + p^2 (L_1 + L_2)^2}} \sin (p\,t + \theta_1);$$

$$(2) \qquad i_2 = \frac{I\sqrt{R_1^2 + p^2 L_1^2}}{\sqrt{(R_1 + R_2)^2 + p^2 (L_1 + L_2)^2}} \sin (p\,t + \theta_2);$$

where, according to Figure 1, R_1 and R_2 are the resistances; L_1 and L_2 the constant coefficients of self-induction, in the two branches;

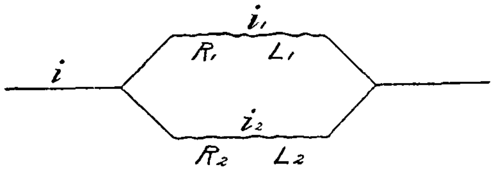

FIG. 1.

$p = 2 \pi n$; I, I_1, and I_2 are the maximum values of i, i_1, and i_2, or the square root of their mean square values multiplied by the square root of 2.* Formulæ (1) and (2) may be written

$$i_1 = I_1 \sin (p t + \theta_1),$$

$$i_2 = I_2 \sin (p t + \theta_1);$$

where

$$(3) \qquad I_1 = \frac{I \sqrt{R_2^2 + p^2 L_2^2}}{\sqrt{(R_1 + R_2)^2 + p^2 (L_1 + L_2)^2}};$$

$$(4) \qquad I_2 = \frac{I \sqrt{R_1^2 + p^2 L_1^2}}{\sqrt{(R_1 + R_2)^2 + p^2 (L_1 + L_2)^2}}.$$

Dividing (3) by (4), we obtain

$$(5) \qquad \frac{I_1}{I_2} = \frac{\sqrt{R_2^2 + p^2 L_2^2}}{\sqrt{R_2^2 + p^2 L_1^2}},$$

whence

$$L_1 = \frac{1}{p} \sqrt{R_2^2 \left(\frac{I_2}{I_1}\right)^2 - R_1^2 + p^2 \left(\frac{I_2}{I_1}\right)^2 L_2^2};$$

and if $L_2 = 0$,

$$(6) \qquad L_1 = \frac{1}{p} \sqrt{R_2^2 \left(\frac{I_2}{I_1}\right)^2 - R_1^2};$$

so that by measuring p, R_1, R_2, and $\frac{I_2}{I_1}$, we can calculate the value of L_1.

Now, considering the practical case, we see that, though the current curve is distorted by the varying permeability of the iron core and the armature reactions of the alternator, yet a definite current passes through each of the two branches, so that equations (5) and (6) still hold, though L_1 is no longer constant throughout an alternation but is the *effective* coefficient of self-induction defined above.

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* See Fleming, Alternate Current Transformer, I. 133.

The practical proof of our conclusion is an easy one. A constant L_1 is measured, first by Rayleigh Bridge and then by our heat method.

The experiment was briefly this. An alternating current was divided between two circuits, both of which had known resistances; one circuit contained a coil with no iron core whose coefficient of self-induction was to be measured; the other branch, for simplicity, had no self-induction. The ratio of the currents was determined by the amounts of heat generated in known parts of the two circuits. The connections are shown in Figure 2.

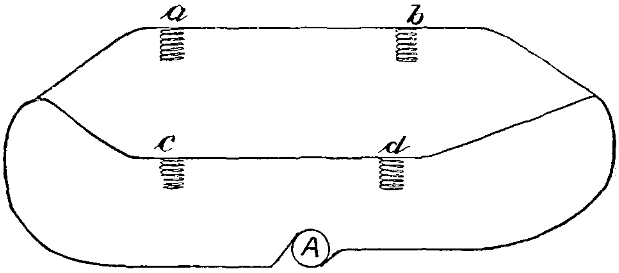

FIG. 2.

A is a suitable alternator, the one used had a frequency of 200 ~. *a* and *c* are heat coils of German silver wire wound non-inductively; the resistance of each was 1.288 ohms, and they were placed in oil in order to measure the heat generated. *b* is the coil whose coefficient of self-induction is to be measured; it had no iron core. *d* is a resistance coil, proportioned to make the currents in the two branches about equal; it was wound non-inductively and placed in oil to keep it cool. A known standard of variable self-induction might be used and would be less trouble to adjust. The heat developed in the two heat coils, was measured by a thermoelectric junction and a delicate galvanometer; one end of the junction was kept in melting ice, and the other end measured the heat of each coil in turn. The quantities of oil in the two were equal, so that the ratio of the galvanometer readings gave the ratio of the heat generated in the two.

We found it desirable to protect our lead-wires from air currents, and to pack the jars containing the heat coils.

The periodicity was measured by taking the speed of the alternator continuously during the test, it being necessary that the speed be constant, or nearly so.

The value of the coefficient of self-induction as measured by a large number of trials with Rayleigh's Bridge and the heat method compared as follows: —

Rayleigh's Bridge.	Heat Method.
.0157 henrys.	.0159 – .0164 henrys.

We then tested the effect of permeability and periodicity by putting an iron core into this same coil. The results were: —

$p = 629$ $L_1 = .066$ henrys.
$p = 1332$ $L_1 = .029$ "

These last results have to be considered with caution, as the impressed electromotive force is changed by changing the periodicity.

This gives an easy practical method of determining the coefficient of self-induction under the ordinary conditions of use, which, so far as we know, none of the various methods attempt to do. The method was suggested by Professor Trowbridge.

JEFFERSON PHYSICAL LABORATORY,
March 1, 1894.

XI.

RESEARCHES ON THE COMPLEX INORGANIC ACIDS.

By Wolcott Gibbs, M. D.,
Rumford Professor Emeritus in Harvard University.

Presented August 1, 1894.

(Continued from Vol. XXI., page 128.)

Platino-Tungstates.

In a notice of these and corresponding compounds of molybdenum published some years since,* and intended to be only preliminary, I pointed out the analogy between them and the silico-tungstates of Marignac. The notice in question requires correction in several particulars, and I shall here give the results of a more complete investigation, conducted with better facilities for work and with a much wider acquaintance with the whole class of complex acids.

Platinic hydrate, like silicic hydrate, dissolves when boiled with solutions of alkaline tungstates belonging to the meta-tungstic series. Platino-tungstates are formed under these circumstances, but various conditions require to be considered. In general I have been accustomed to prepare the hydrate $Pt(OH)_4$ by Frémy's method, that is, by boiling a solution of platinic chloride with a large excess of sodic hydrate for some time and then adding acetic acid in small excess, when the platinic hydrate separates as a pale buff-yellow slimy compound to be washed by repeated decantation with cold water. When the last portions of saline matter have been removed the wash-water becomes turbid and settles only after very long standing. The hydrate obtained in this way sometimes dissolves very readily in hot solutions of alkaline tungstates, sometimes only after long boiling, and sometimes is almost insoluble. The process is therefore an uncertain one at best. The platino-tungstates formed have a yellow or orange-yellow color and in many cases crystallize well. By the process which I have given it is usually difficult to obtain perfectly saturated compounds unless a rather large excess of platinic hydrate is employed. When this is the case a greater or less quantity of a deep orange-red solution is sometimes formed, which on standing deposits a dark tarry mass in case the sodic tungstate is employed. In place of sodic hydrate I have also used baric hydrate in preparing a soluble form of the platinum compound, but in this case also the platinic hydrate, according to varying conditions, varied very much in solubility.

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* Berichte der deutschen chemischen Gesellschaft, X. 1384. 1877.

When platinic hydrate is boiled with a solution of 10 : 4 sodic tungstate the latter being in large excess, yellow solutions are sometimes formed which on evaporation and standing yield large crystalline masses with a fine yellow color and strong lustre. These crystals consist essentially of the 10 : 4 sodic salt, $10\ WO_3 . 4\ Na_2O + 23$ aq., but they contain a greater or less proportion of a platinic compound which — water of crystallization apart — has probably the formula $10\ WO_3 . PtO_2 . 4\ Na_2O$, and which appears to be isomorphous with the tungstate. A compound of this kind gave on analysis figures which corresponded very closely with the formula,

$$10\ WO_3 . PtO_2 . 4\ Na_2O + 2\ \{10\ WO_3 . 4\ Na_2O\} + 72 \text{ aq.}$$

We may have here a combination of two isomorphous salts, having respectively the formulæ, $10\ WO_3 . PtO_2 . 4\ Na_2O + 26$ aq., and $10\ WO_3 . 4\ Na_2O + 23$ aq. The analyses of two different preparations of the salts correspond very closely.

The difficulty of obtaining definite compounds by direct solution of platinic hydrate led me to another method, which may be used with much advantage. Pure crystallized sodic tungstate is to be dissolved in water, a rather large excess of sodic hydrate added, and a neutral or nearly neutral solution of platinic chloride added to the boiling solution in small portions at a time. Platinic hydrate is formed and instantly dissolved. The chloride is to be added until a distinct excess of $Pt(OH)_4$ is present. Acetic acid is then to be added in small excess. Alcohol then often throws down a dark tarry mass which contains one or more saturated platino-tungstates. When the proportion of platinic chloride necessary happens to be exact, a beautiful orange-colored clear solution is formed which on cooling or evaporation deposits an abundance of beautiful yellow needles or prisms easily purified by recrystallization. By this process a definite salt may be prepared in a very short time and in large quantity. Different salts are, however, formed under different conditions, and further investigations must show whether it is possible by using definite quantities of platinic chloride and of sodic tungstate to obtain uniform results as regards the constitution of the salt formed. It is indispensable to employ pure platinic chloride or chlorplatinates. Even traces of iridium give a greenish tint to the platino-tungstates formed, a fact which misled me in my earlier experiments. Contrary to my preliminary statement, I now find, on more prolonged study, no isomeric platino-tungstates.

10 : 1 : 6 *Sodic Platino-tungstate.* 12 : 5 sodic tungstate very readily dissolves platinic hydrate in its soluble form, and gives a fine deep orange-colored solution which on standing yields a mass of ill defined dull orange crystals. These may be redissolved, recrystallized, and dried on woollen paper. Of these crystals:

1.1460 grams gave 0.8430 gram $Pt + WO_3$ = 73.56 per cent.
1.1806 grams gave 0.0686 gram $Pt + WO_3$ = 73.57 "
1.1806 grams gave 0.0706 gram platinum = 5.98 "
1.1460 grams gave 0.8695 gram platinum = 6.06 "
1.8770 grams gave 0.7774 gram WO_3 = 67.83 "
0.8770 gram lost on ignition 0.1397 gram oxygen and water,
= 15.93 per cent.

The analyses lead to the formula,

$$10\ WO_3 \,.\, PtO_2 \,.\, 6\ Na_2O + 28\ aq.,$$

which requires: —

		Calculated.		Mean.		Found.			
10 WO_3	2320	67.79	74.40	67.65	74.65	67.56	67.83	67.57	
PtO_2	226.5	6.61		7.00		6.96	7.05		
6 Na_2O	372	10.87	25.60				10.51		25.45
28 H_2O	504	14.73					14.94		
	3422.5	100.00							

The soda being estimated by difference. It is remarkable that this salt contains six molecules of base instead of four, all known silico-tungstates being tetrabasic. The solution of this salt when shaken with a solution of potassic bromide gives an amorphous pasty mass with a deep orange-red color. In the analysis of this class of compounds it is best to determine the platinum by ignition with sodic carbonate. On treatment of the fused mass with water, the platinum remains as metal, and the tungsten may then be determined in the filtrate in the usual manner. Nearly all the analyses were made in this way, sodic oxide being determined by difference. In some cases, however, tungstic and platinic oxides were precipitated together by mercurous nitrate and mercuric oxide.

20 : 1 : 9 *Sodic Platino-tungstate.* In one experiment in which I boiled a portion of pure sodic tungstate with a considerable excess of sodic hydrate, and added to the boiling solution chlorplatinic acid ($PtCl_6H_2$) in small portions at a time, a fine yellow solution was formed, after addition of an excess of acetic acid, which soon deposited a mass of topaz-yellow crystals. This could be redissolved and recrystallized without decomposition. The mother liquor appeared to contain one or two other salts. Of this salt:

(1) 1.4847 grams lost on ignition 0.2453 gram = 16.52% O + H_2O.
(4) 1.4154 grams lost on ignition 0.2349 gram = 16.61% O + H_2O.
(2) 1.4847 grams gave 0.0466 gram platinum = 3.73% PtO_2.
(3) 1.0976 grams gave 0.0345 gram platinum = 3.65% PtO_2.
(5) { 1.4154 grams gave 1.0467 grams platinum = 3.83%.
{ 1.4154 grams gave 1.0129 grams WO_3 = 71.57%.
(6) 1.4847 grams gave 1.0619 grams WO_3 = 71.50%.

The analyses lead to the formula,

$$20\ WO_3 \,.\, PtO_2 \,.\, 9\ Na_2O + 58\ aq.,$$

which requires:

		Calculated.	Mean.	Found.		
20 WO_3	4640	71.73	71.53	71.57	71.50	
PtO_2	226.5	3.50	3.74	3.73	3.65	3.83
9 Na_2O	558	8.63	8.68		8.67	
58 H_2O	1044	16.14	16.05	16.00	16.09	
	6468.5	100.00				

The solution of this salt has a strongly acid reaction with litmus. It gives with ammonic chloride beautiful colorless scaly crystals, slightly soluble in cold but soluble in boiling water, exactly resembling in appearance the sodio-ammonic tungstate, 12 $WO_3 \,.\, Na_2O \,.\, 4\ (NH_4)_2O$, and containing no platinum. This reaction seems to support the view that the compound is a double salt, and we may perhaps assume that it is represented by the formula,

$$10\ WO_3 \,.\, 4\ Na_2O + 10\ WO_3 \,.\, PtO_2 \,.\, 5\ Na_2O + 58\ aq.$$

The principal reactions of this salt are as follows: —

With $AgNO_3$ a white fine grained crystalline precipitate settling slowly.
With $TlNO_3$ a similar precipitate in rather coarser grains.
With SO_4Cu a very pale blue or bluish white fine grained precipitate.
With $HgNO_3$ a bright yellow amorphous precipitate.
With $Co(NH_3)_6Cl_3$ a pale buff precipitate quickly becoming crystalline in leaves.

A quantity of this platino-tungstate was precipitated by a solution of mercurous nitrate. The fine yellow mercurous salt was well washed and then decomposed by dilute chlorhydric acid, the platino-tungstate being in very small excess. The clear yellow filtrate on spontaneous evaporation deposited a pale yellow substance which may prove to be the corresponding acid.

30 : 2 : 15 *Sodic Platino-tungstate.* This salt was obtained under the same conditions as the last, and formed granular efflorescent dull yellowish crystals readily soluble in water. Of this salt:

1.3231 grams gave 0.9787 gram $WO_3 + Pt$ = 73.97 per cent.
1.3231 grams gave 0.0510 gram platinum = 4.49 per cent PtO_2.
1.0144 grams gave 0.0410 gram platinum = 4.70 per cent PtO_2.
1.5776 grams lost on ignition with WO_4Na_2 0.2657 gram $O + H_2O$ = 16.71 per cent.
1.5776 grams gave 1.1059 grams WO_3 = 70.06 per cent.
1.3231 grams gave 0.9271 gram WO_3 = 70.03 per cent.

The analyses lead to the formula,

$$30\ WO_3 . 2\ PtO_2 . 15\ Na_2O + 89\ aq.,$$

which requires:

		Calculated.	Found.	
30 WO_3	6960	69.98	70.03	70.06
2 PtO_2	453	4.56	4.49	4.70
15 Na_2O	930	9.35	9.24	
89 H_2O	1602	16.11	16.18	
	9945			

A solution of this salt also gives white scaly crystals with potassic and ammonic salts. It gives a white flocky precipitate with baric chloride, and a pale yellow flocky crystalline precipitate with mercurous nitrate. The compound is probably, like the last described, a double salt and may have the formula,

$$10\ WO_3 . 3\ Na_2O . H_2O + 2\ \{10\ WO_3 . PtO_2 . 6\ Na_2O\} + 88\ aq.$$

The solution of the salt is acid to litmus. Analysis by Dr. Morris Loeb.

30 : 1 : 12 *Sodic Platino-tungstate.* I obtained this salt by boiling platinic hydrate with 10 : 4 sodic tungstate for some time in a platinum vessel. It formed very large masses of honey-yellow heavy crystals, very easily soluble in water. Of this salt:

1.1441 grams lost on gentle heating 0.1583 gram water = 13.84%.
0.9383 gram lost on gentle heating 0.1313 gram water = 13.99%.
1.8069 grams gave 1.4033 grams $WO_3 + Pt = 77.66\%$.
0.8809 gram gave 0.6847 gram $WO_3 + Pt = 77.72\%$.
* —— gram gave —— gram platinum = 2.46% PtO_2.

The analyses agree with the formula,

$$30\,WO_3 . PtO_2 . 12\,Na_2O + 72\text{ aq.},$$

which requires:

		Calculated.	Found.	
$30\,WO_3$	6960	75.44	75.53	75.43
PtO_2	226.5	2.45	2.46	
$12\,Na_2O$	744	8.06	8.15	
$72\,H_2O$	1296	14.05	13.84	13.99
	9226.5	100.00		

In the analyses the water was determined by heating in an air-bath, and not by ignition. No correction for oxygen of PtO_2 is therefore applied. The solution of the salt gives the characteristic white scaly crystals with NH_4Cl and KCl, and as in the last two cases we may safely assume that the compound is a double salt. The most probable formula considering the mode of formation is,

$$10\,WO_3 . PtO_2 . 4\,Na_2O + 2\,\{10\,WO_3 . 4\,Na_2O\} + 72\text{ aq.}$$

From the above it appears that, strictly speaking, none of the compounds described correspond to the silico-tungstates of Marignac, all of which appear to contain four molecules of basic oxide. Such platinum compounds may, however, exist in combination, as seems to be shown in the salts last described.

The other metals of the platinum group will probably be found to form similar compounds. Want of material has prevented a careful study of the subject, but a number of qualitative tests made with small quantities of salts of iridium, ruthenium, palladium, and osmium appeared to show clearly that these metals also form compounds with tungstic and molybdic oxides analogous to those of platinum.

8 : 2 : 3 *Platino-molybdate of Ammonium.* When freshly prepared sodic platinate $Na_2O . 3\,PtO_2$ is boiled with a solution of 14 : 6 ammonic molybdate, it readily dissolves to an orange-yellow liquid, which after a time deposits beautiful lemon-yellow crystals, which may be easily purified by recrystallization. The salt dissolves rather easily in

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* The data of this analysis were accidentally lost.

cold, and very readily in hot water. The solution gives with argentic nitrate a pale yellow flocky precipitate which becomes crystalline on standing. With mercurous, mercuric, and thallous nitrates it gives pale yellow flocky precipitates not distinctly crystalline and settling quickly. With nitrate of croceo-cobalt the solution gives a beautiful bright yellow crystalline salt. The formula of the ammonium salt is,

$$8\,MoO_3 \cdot 2\,PtO_2 \cdot 3(NH_4)_2O + 12\ aq.,$$

as the following analyses show:

1.7831 grams gave 0.3554 gram Pt = 19.94% = 23.21% PtO_2.
0.5425 gram gave 0.1075 gram Pt = 19.82% = 23.09% PtO_2.
0.4354 gram gave 0.0868 gram Pt = 19.92% = 23.15% PtO_2.
1.0407 grams gave 0.0535 gram NH_3 = 5.14%.
0.5149 gram gave 0.0405 gram NH_3 = 5.14%.
0.5878 gram gave 0.0459 gram NH_3 = 5.14%.
1.2015 grams lost on ignition with WO_4Na_2 0.2663 gram 22.17% $H_2O + NH_3 + O$.
0.8368 gram lost on ignition with WO_4 0.1876 gram 22.42% $H_2O + NH_3 + O$.

		Calculated.	Mean.	Found.		
8 MoO_3	1152	58.27	57.83			
2 PtO_2	453	22.91	23.15	23.21	23.09	23.15
6 NH_3	102	5.16	5.14	5.14	5.14	5.14
15 H_2O	270	13.66	13.88	13.76	14.01	
	1977	100.00				

Other salts of this series may be prepared from the ammonium salt by precipitating its solution with mercurous nitrate and decomposing the well washed mercurous salt by solutions of the chlorides of other metals.

4 : 2 : 2 *Platino-molybdate of Ammonium.* The solution from which the yellow ammonium salt first described separated by crystallization gave on evaporation a dark colored liquid over a heavy oily deep brown-red substance. This last was washed with a little ice-cold water and gradually dried to a transparent dark brown-red mass which broke up into clean sharp brilliant fragments. Of this salt:

0.4502 gram lost on careful heating 0.1297 gram = 28.81% $H_2O + NH_3 + O$.
0.4502 gram gave 0.1226 gram platinum = 31.63% PtO_2.
0.5398 gram gave 0.0402 gram $(NH_4)_2O$ = 4.91% NH_3.
0.4917 gram gave 0.0369 gram $(NH_4)_2O$ = 4.87% NH_3.

The analyses lead to the formula,

$$4\ MoO_3 \, . \, 2\ PtO_2 \, . \, 2\ (NH_4)_2O + 19\ aq.,$$

which requires:

		Calculated.	Found.	
4 MoO_3	576	40.03	39.56	
2 PtO_2	453	31.48	31.63	
4 NH_3	68	4.72	4.91	4.87
19 H_2O	342	23.77	23.97	
	1439	100.00		

As in the last case the molybdic oxide is estimated by difference which in the present state of our knowledge of analysis is the most accurate method. The salt can hardly have been absolutely pure. Water decomposes it and gives an opaque buff-yellow compound which I have not examined. It will be seen from the above that the platino-molybdates described do not correspond in general composition with the only silico-molybdates known in which the ratio of molybdic to silicic oxide is as 12 : 1.

Rammelsberg* has described a molybdate of the dioxide and ammonium which has the formula,

$$4\ MoO_3 \, . \, 2\ MoO_2 \, . \, (NH_4)_2O + 9\ aq.$$

In endeavoring to prepare a class of stanno-tungstates I obtained a sodium salt the solution of which gave on evaporation a hard nearly colorless glassy mass. This gave on analysis results which did not correspond very well, but the mean of several led to the formula,

$$4\ WO_3 \, . \, 2\ SnO_2 \, . \, Na_2O + 7\ aq.$$

The compound deserves further study, and is not without interest in connection with the two salts noticed above.

60 : 1 : 10 *Platino-molybdate of Potassium.* This salt was obtained by boiling potassic molybdate with an excess of potassic hydrate, and adding a solution of $PtCl_6H_2$ until platinic hydrate which at first dissolves as fast as formed, was in small excess. Acetic acid was then added to an acid reaction. On standing fine granular yellow crystals were formed in quantity. These were dissolved in hot water and recrystallized. Of this salt:

0.5191 gram gave 0.0098 gram Pt = 2.20% PtO_2.
0.5191 gram gave 0.5665 gram MoS_3 = 81.85% MoO_3.

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* Poggendoff, Annalen, CXXVII. 291.

0.6459 gram lost on ignition with WO_4Na_2 0.0447 gram = 6.92% $O + H_2O$ = 6.61 H_2O.
1.2241 grams lost on ignition with WO_4Na_2 0.0872 gram = 7.12% $O + H_2O$ = 6.81 H_2O.

The analyses lead to the formula,

$$60\,MoO_3 \cdot PtO_2 \cdot 10\,K_2O + 40\,aq.,$$

which may be written provisionally as

$$12\,MoO_3 \cdot PtO_2 \cdot 2\,K_2O \cdot 4\,H_2O + 4\,\{12\,MoO_3 \cdot 2\,K_2O \cdot 3\,H_2O\} + 24\,aq.$$

The formula requires:

		Calculated.	Found.	
60 MoO_3	8640	82.04	81.85	
PtO_2	226.5	2.16	2.20	
10 KO_2	994	8.97	9.24	
40 H_2O	720	6.83	6.61	6.81
	10580.5	100.00		

This salt is readily soluble in hot water without apparent decomposition. It gives a very pale yellow crystalline precipitate with argentic nitrate and a pale greenish blue precipitate with cupric sulphate, which is soluble in an excess of this last.

Rosenheim has recently described* another platino-tungstate with the empirical formula,

$$7\,WO_3 \cdot 2\,PtO_2 \cdot 5\,Na_2O + 35\,aq.,$$

and regards it as a double salt,

$$7\,WO_3 \cdot 3\,Na_2O + 2\,\{PtO_2 \cdot Na_2O\} + 35\,aq.$$

This salt was obtained by boiling normal sodic tungstate, WO_4Na_2, in concentrated solution with platinic hydrate, and presented small yellow needles which could not be recrystallized without decomposition. He did not succeed in obtaining platino-tungstates by boiling platinic hydrate with various meta-tungstates, and suggests that the three salts which I described in my preliminary notice were mixtures of meta-tungstates (para-tungstates) and platinic oxide. They were, on the contrary, perfectly well defined and crystallized, as were also the platino-tungstates and platino-molybdates described in this paper. Further investigation will probably show that a number of other salts can be obtained by the method which I have described in which the platinic hydrate is brought in contact with acid tungstates or molybdates in the nascent state. Phospho-platino-tungstates and similar molybdenum compounds appear also to exist. A solution of 24 : 1 : 2 phospho-tungstate of sodium readily dissolves platinic hydrate on boiling, and gives an orange-colored solution which after filtration and evaporation deposits ill defined orange crystals. When a solution of ammonic chloride is mixed with the solution obtained as above, a beautiful orange crystalline salt is thrown down. In a preliminary notice published in 1877,* I have described the preparation and properties of platino-tungstates having respectively the formulas

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* Berichte der deutschen chem. Gesellschaft, XXIV. 2397.

$$10\,WO_3 . PtO_2 . 4\,Na_2O + 25\text{ aq}; \quad 10\,WO_3 . PtO_2 . 4\,K_2O + 9\text{ aq.};$$
$$10\,WO_3 . PtO_2 . 4\,(NH_4)_2O + 12\text{ aq.};$$

and of a platino-molybdate with the formula

$$10\,MoO_3 . PtO_2 . 4\,Na_2O + 29\text{ aq}.$$

All of these tungstate compounds were obtained by boiling

$$10\,WO_3 . 4\,Na_2O + 23\text{ aq}.$$

with the soluble form of platinic hydrate. The molybdenum compound was obtained in a similar manner, but I am not now able to state what acid molybdate of sodium was employed. I have not succeeded in obtaining these compounds a second time, and in the long interval of time which has elapsed since the publication of my preliminary notice the notes of description and analyses have been lost. I can only express my conviction that more extended investigations will show that no error has been made, and that the compounds unite as described. I will further remark, that, taking the analyses which I have given in this paper, it may be possible to give simpler formulas for some at least of the salts described. The formulas given represent I believe most accurately the results of the analyses, but as the percentages of platinum are relatively small the quotients of these percentages by the atomic mass of platinum are very small divisors. On the other hand, the quotients obtained by dividing the percentages of tungstic or molybdic oxide by the molecular masses of tungstic or molybdic oxide are relatively very large, and the ratio between the two quotients in question becomes somewhat uncertain. The compounds which I have obtained by the method which I have given of bringing platinic oxide *in statu nascenti* into contact with the solutions of acid tungstates or molybdates gives such well defined and beautifully crystalline salts that the subject will doubtless attract the attention of other chemists. I will make the suggestion that possibly the salts which I described in my preliminary notice may be obtained by adding ammonic chloride to solutions of the double salts described in this paper, so as, in the case of the tungstic compounds at least, to precipitate the tungstic oxide not combined with platinic oxide in the form of

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* Berichte der deutschen chem. Gesellschaft, X. 1384. Am. Journ. of Science, [3.], XIV. 61.

$$10\,WO_3 . 4\,Na_2O + 4\,\{10\,WO_3 . 4\,(NH_4)_2O\} + 50\text{ aq.},$$

or an analogous salt. The solution should then contain only a platino-tungstate. The application to the platino-molybdates described is less probable.

SECOND SERIES OF PYROPHOSPHO-TUNGSTATES AND PYROPHOSPHO-MOLYBDATES.

When sodic pyrophosphate is added in excess to a solution containing a metallic salt, the precipitate which is at first found is in many cases redissolved with formation of a double salt of sodium and the metal in question. In a certain number of cases, the heavier metal in the new compound is not replaceable under ordinary conditions, and does not exhibit its characteristic reactions with tests. These facts are of course familiar to all chemists. Persoz supposed that these salts might be represented, in the case of divalent metals, by the general formula, as we should now write it,

$$P_2O_7R'' + P_2O_7Na_4,$$

and that the group P_2O_7R'' was to be regarded as electro-negative to the group $P_2O_7Na_4$, so that the compound would be simply analogous to ClNa. If we write the double salt $P_2O_7R''Na_2$, we may regard the complex P_2O_7R'' as playing the part of a relatively electro-negative group, as in the case of double cyanides, so called. Whether this view is to be considered as identical with that of Persoz, is a question about which opinions may differ, and which is not important for my present purpose. Admitting that the groups P_2O_7R'' or P_2O_7R''' are transferable as such in their relatively simple alkaline salts, we may inquire whether they enter into the composition of complex acids, and if so, whether the compounds so formed differ from ordinary pyrophospho-tungstates and pyrophospho-molybdates. As the initial point in this investigation I have selected mangano-disodic pyrophosphate, $P_2O_7Mn_2Na_2$.

Mangano-sodic Pyrophospho-Molybdate.

In another part of this memoir I have described several salts belonging to the group of pyrophospho-tungstates. As these were peculiar in their constitution, it became a matter of interest to determine whether the pyrophospho-molybdates had a similar constitution, or, in other words, whether they contained the pyrophosphoric group $22\ RO_3 . 9\ P_2O_7$ found in the salts of the tungstic series.

Molybdic teroxide boiled with sodic pyrophosphate, care being taken to keep the oxide in excess, is dissolved with much facility and in large quantity. The colorless solution may be evaporated to a syrup without yielding crystals on standing, and gives no precipitates with salts of potassium or ammonium. The solution, however, gives precipitates with salts of most of the heavier metals. Of these I selected the manganous compounds for special study, supposing that all the manganese would be present as base, and that a comparison could be made between salts of this type and those in which manganese exists in the pyrophosphoric molecule, and which I shall describe further on.

When a solution of manganous chloride is mixed with one of sodic pyrophospho-molybdate prepared as above, a dull buff-colored apparently amorphous precipitate is formed. On standing with an excess of the sodium salt, this was gradually converted into a mass of beautiful bright yellow crystals. These were well washed with cold water, and then dissolved in boiling water. The filtered solution gave on cooling a mass of sulphur-yellow crystals, which were again dissolved and recrystallized. The salt was then dried on woollen paper. It was analyzed by Mr. G. W. Patterson.

$$\left\{\begin{array}{l}1.3289 \text{ grams gave } 0.1065 \text{ gram } P_2O_7Mg_2 = 5.13\%\ P_2O_5.\\ 1.3289 \text{ grams gave } 0.2486 \text{ gram } P_2O_7Mn_2 = 9.36\%\ MnO.\end{array}\right.$$

$$\left\{\begin{array}{l}0.9538 \text{ gram gave } 0.1819 \text{ gram } P_2O_7Mn_2 = 9.53\%\ MnO.\\ 0.9538 \text{ gram gave } 0.5934 \text{ gram } P_2O_5 + MoO_3 = 62.22\%.\end{array}\right.$$

1.0960 grams lost with Wo_4Na_2 0.2037 gram = 18.56%.
0.9445 gram lost with Wo_4Na_2 0.1743 gram = 18.45%.

The analyses lead to the formula

$$22\ MoO_3 . 2\ P_2O_5 . 7\ MnO . 9\ Na_2O + 57\ aq.,$$

which requires :

		Calculated.		Found.	
22 MoO_3	3168	57.26	62.39	57.16	62.29
2 P_2O_5	284	5.13		5.13	
7 MnO	497	8.99	19.07	9.36	19.20
9 Na_2O	558	10.08		9.84	
57 H_2O	1026	18.54		18.58	18.45
	5533	100.00			

The salt is nearly insoluble in cold water. Boiling water dissolves it, but the salt is decomposed, giving a pale yellow flocky precipitate and a sherry-wine colored solution. On standing a short time, the solution as it cools becomes pale yellow, and finally almost colorless, while the precipitate gradually becomes brighter yellow and crystalline, and the original salt appears to be again formed by recombination. Both the precipitate formed in the decomposition by boiling water and the wine-yellow solution give reactions with argentic nitrate which differ from one another as well as from the yellow crystalline silver salt formed by digesting the pyrophospho-molybdate of manganese and sodium with argentic nitrate.

In the analysis the solution of the salt was boiled with mercurous nitrate and mercuric oxide. The precipitate contained only molybdic and phosphoric oxides, and was free from manganese. There is therefore reason for assuming, as I have done, that all the manganese is basic, and that none is present in the form of the molecule P_2O_7Mn.

Mangano-ammonic Pyrophospho-Molybdates.

When manganous pyrophosphate is digested for some time with a strong solution of 14 : 6 acid ammonic molybdate, a buff-yellow very slightly soluble compound is formed. This is to be well washed, dried on woollen paper, and afterward *in pleno* over sulphuric acid. Of this salt, analyzed by Mr. G. W. Patterson:

0.7830 gram lost on ignition with WO_4Na_2 0.0778 gram $NH_3 + H_2O = 9.94\%$.
0.6554 gram lost on ignition with WO_4Na_2 0.0645 gram $NH_3 + H_2O = 9.84\%$.
0.8590 gram gave 0.0338 gram $NH_3 = 3.92\%$.
0.7191 gram gave 0.0285 gram $NH_3 = 3.97\%$.
$\begin{cases} \text{0.8725 gram gave 0.0881 gram } P_2O_7Mg_2 = 6.46\%\ P_2O_5. \\ \text{0.8725 gram gave 0.2841 gram } P_2O_7Mn_2 = 12.62\%\ MnO. \end{cases}$

The analyses lead to the formula,

$$20\,MoO_3 \,.\, 2\,P_2O_5 \,.\, 10\,MnO \,.\, 5\,(NH_4)_2O + 10\,aq.,$$

which requires:

		Calculated.		Found.	
20 MoO_3	2880	66.76	73.34	67.27	73.73
2 P_2O_5	284	6.58		6.46	
10 MnO	710	16.46		16.30	
10 NH_3	170	3.94		3.92	3.97
15 H_2O	270	6.26		5.94	
	4314	100.00			

In the analyses the salt was digested for some time at a boiling heat with mercurous nitrate and mercuric oxide. The mercurous salt formed contained manganous oxide. The precipitate was fused with a mixture of potassic and sodic carbonates to separate manganous oxide. The filtrate from this last gave the phosphoric pentoxide. Molybdic teroxide was determined by difference. As the salt could not be recrystallized, the defects in the analysis are doubtless chiefly due to traces of impurity. The formula of the salt should be written, according to my view:

$$20\,MoO_3 \,.\, 2\,P_2O_7Mn \,.\, 2\,(NH_4)_2O \,.\, 8\,MnO \,.\, 3\,(NH_4)_2O + 12\,aq.$$

We may have here a double salt, as, for instance,

$$10\,MoO_3 \,.\, P_2O_7Mn(NH_4)_2 \,.\, 4\,MnO \,.\, (NH_4)_2O \,.\, H_2O$$
$$+\; 10\,MoO_3 \,.\, P_2O_7Mn(NH_4)_2 \,.\, 4\,MnO \,.\, 2\,(NH_4)_2O + 12\,aq.,$$

but of course other arrangements are possible.

The manganese in the molecule containing P_2O_7 may be called, for convenience, the internal or fixed manganese. to distinguish it from the external or basic manganese. To determine if possible the ratio between the external and internal manganese, I digested a weighed portion of the salt in the cold for twelve hours with mercurous nitrate, and then boiled, adding a little mercuric oxide in the usual manner. In the filtrate, after separating the mercury, the manganese was determined as $P_2O_7Mn_2$. In this manner,

$$1.2306 \text{ grams gave } 0.3520 \text{ gram } P_2O_7Mn = 11.08\,\%.$$

From this it appears that about $\frac{1}{12}$ of the manganese was precipitated by mercurous nitrate, in place of $\frac{8}{10}$. If, therefore, we consider $\frac{2}{10}$ of the manganese to be present in the salt as P_2O_7Mn, we must suppose that this molecule is broken up. to a certain extent at least, by boiling with mercurous nitrate, and it is very doubtful whether the manganous oxide exists in any other form than as a base. Certainly there is no sufficient evidence that it forms here an integrant molecule P_2O_7Mn, as in sodio-manganous pyrophosphate, $P_2O_7Mn . Na_2$. I regard the question, however, as still an open one, since the molecule P_2O_7Mn, assuming its existence, may be decomposed by mercurous nitrate and give a corresponding mercurous integrant molecule $P_2O_7Hg_2$, and since the salt is decomposed by water like the other salts of this series. It appears also from the above that the pyrophospho-molybdates do not correspond in composition to the pyrophospho-tungstates. At least I have not found in them the molybdenum molecule corresponding to the tungstic molecule, $22\ WO_3 . 9\ P_2O_7$. It must, however, be remarked that, as I shall show, the pyrophospho-tungstates which contain manganese do not contain this molecule.

Mangano-sodic Pyrophospho-Tungstates.

These salts are very easily formed by boiling manganous pyrophosphate with acid tungstates. Dark sherry-wine colored solutions are formed, which in cooling deposit crystals in abundance.

14 : 1 : 3 : 6 *Mangano-sodic Pyrophospho-Tungstate.* This salt is formed more conveniently by mixing a solution of 12 : 5 sodic tungstate with manganous pyrophosphate and digesting for some hours in a closed bottle heated in a water bath. The pyrophosphate must be in excess. It dissolves rather slowly to a fine deep orange-colored liquid, which after evaporation deposits beautiful crystals, which may be redissolved and recrystallized. In spite of the employment of an excess of manganous pyrophosphate, it is rather difficult to obtain a solution of the salt which is perfectly saturated with the manganous salt. The crystals have a brownish orange color. They effloresce in dry air, though not rapidly, but *in pleno* over sulphuric acid they lose water in relatively large quantity. Of this salt, analyzed by Mr. G. W. Patterson:

1.4176 grams lost on ignition with WO_4Na_2 0.2032 gram = 14.34% water.

1.2375 grams gave 0.0611 gram $P_2O_7Mg_2$ = 3.16% P_2O_5.

$\left\{\begin{array}{l}\text{1.0476 grams gave 0.1041 gram } P_2O_7Mn_2 = 4.97\%\ MnO. \\ \text{1.0476 grams gave 0.7650 gram } WO_3 + P_2O_5 = 73.05\%.\end{array}\right.$

The analyses lead to the formula,

$$14\ WO_3 . P_2O_5 . 3\ MnO . 6\ Na_2O + 36\ aq.,$$

which requires:

		Calculated.		Found.	
14 WO_3	3248	70.25	73.32	69.89	73.05
P_2O_5	142	3.07		3.16	
3 MnO	213	4.62	12.66	4.97	12.65
6 Na_2O	372	8.04		7.68	
36 H_2O	648	14.02		14.34	
	4623	100.00			

We may give this salt the formula

$$14\,WO_3\,.\,6\,Na_2O + P_2O_8Mn_3 + 36\text{ aq.},$$

if we suppose that the pyrophosphate of manganese has become orthophosphate. Both constituents are then normal salts.

The ammonium salt was prepared by double decomposition between the sodium salt and ammonic chloride, and repeated crystallization. It presented orange-colored prismatic crystals, very soluble in both hot and cold water. Of this salt:

0.7846 gram gave 0.01715 gram $NH_3 = 2.19\%$.
0.6556 gram gave 0.01394 gram $NH_3 = 2.13\%$.
0.4886 gram gave 0.0594 gram $NH_3 + H_2O = 12.16\%$.
1.0895 grams gave 0.1162 gram $P_2O_7Mn_2 = 5.83\%$ MnO.

The analyses correspond well with the formula,

$$28\,WO_3\,.\,2\,P_2O_5\,.\,6\,MnO\,.\,5\,(NH_4)_2O\,.\,2\,Na_2O + 48\text{ aq.},$$

which requires:

		Calculated.	Mean.		
28 WO_3	6496	77.67	77.76	77.84	77.69
2 P_2O_5	284	3.40	3.13	3.13	
6 MnO	426	5.09	5.39	5.33	5.45
10 NH_3	170	2.03	2.16	2.13	2.19
2 Na_2O	124	1.48	1.56	1.56 (diff.)	
48 H_2O	864	10.33	10.00	10.00	
	8364	100.00			

We may formulate this salt as

$$\{14\,WO_3\,.\,4\,MnO\,.\,2\,Na_2O + P_2O_7Mn_2\} + \{14\,WO_3\,.\,5\,(NH_4)_2O\,.\,H_2O + P_2O_7H_4\} + 45\text{ aq.},$$

the type being $14\,WO_3\,.\,6\,RO + P_2O_7R'_4$, so that so far as the empirical constitution is concerned the salt may be regarded as a double salt of two normal constituents. The analyses were made by Mr. G. W. Patterson.

Auramin Pyrophosphates.

When a solution of double chloride of gold and sodium $AuCl_4Na$ is made as nearly neutral as possible and then boiled with sodic pyrophosphate $P_2O_7Na_4$, a very pale yellow solution is formed, which contains the auro-sodic salt discovered by Persoz, the formula of which we should now write $P_2O_7Au'''Na$. The solution of this salt gives with ammonia a white precipitate which quickly becomes yellow and crystalline. With argentic nitrate it gives a pale yellow flocky crystalline precipitate, which is very insoluble and does not blacken readily in the light. With mercurous nitrate it gives a greenish gray flocky crystalline precipitate. A nearly white curdy precipitate is formed with sulphate of luteo-cobalt; none with sulphate of croceo-cobalt. With $Pt(NH_3)_4Cl_2$ gold is reduced.

The crystalline precipitate formed by ammonia in the auro-sodic pyrophosphate solution was well washed, dried at 150°, and analyzed.

0.9665 gram gave 0.6756 gram gold = 78.44% Au_2O_3.
0.9031 gram gave 0.7003 gram gold = 78.34% Au_2O_3.
0.9665 gram gave 0.1621 gram $P_2O_7Mg_2$ = 10.73% P_2O_5.
1.0031 grams gave 0.1703 gram $P_2O_7Mg_2$ = 10.86% P_2O_5.
0.7375 gram gave 0.02286 gram NH_3 = 3.10%.
0.7691 gram lost, at 150° C., 0.0420 gram water = 5.46%.

The analyses lead to the formula

$$14\,Au_2O_3 \,.\, 6\,P_2O_5 \,.\, 14\,NH_3 \,.\, 3\,Na_2O + 24\,Aq.,$$

which requires:

		Calculated.	Found.	
$14\,Au_2O_3$	6178	78.34	78.44	78.34
$6\,P_2O_5$	852	10.80	10.73	10.86
$14\,NH_3$	238	3.02	3.10	
$3\,Na_2O$	186	2.36	2.26 (diff.)	
$24\,H_2O$	432	5.48	5.46	
	7886	100.00		

The analysis is due to Dr. Morris Loeb, who assisted me in this part of my work most efficiently.

The salt does not explode at low temperatures, but on heating to a little above 170° C. a violent explosion takes place. This shows clearly that part at least of the gold is in the form of an auramin, or compound with ammonia.

The auramin pyrophosphate of sodium, on boiling with baric chloride, gives a yellow crystalline salt; with mercuric chloride, a fine pale yellow crystalline salt which becomes very distinct on boiling.

When the auramin salt is boiled with mercurous nitrate, some mercury is reduced to metal, and at the same time very characteristic white prismatic crystals are formed. Chlorhydric acid does not sensibly dissolve the pyrophosphate, but changes it to a pale yellow flocky crystalline body. Chloride of luteo-cobalt gives on boiling an orange crystalline salt.

When the crystalline yellow or dull orange baric salt is well washed with hot water and then filtered off, the colorless filtrate on evaporation gives with sodic hydrate a very distinct reaction for ammonia. Part of the ammonia in the salt must therefore have been in the form of ammonia, unless we admit that the auramin is decomposed under the circumstances. When treated with a cold solution of argentic nitrate reaction sets in at once, and a fine yellow flocky crystalline salt is formed; but no trace of ammonia is obtained from the filtrate after washing the salt with cold water and separating the excess of silver. Both the barium and silver salts were partially analyzed.

The barium salt was analyzed by Mr. G. W. Patterson :

0.6472 gram gave 0.1015 gram $BaSO_4$ = 10.30% BaO.
0.6472 gram gave 0.1426 gram $P_2O_7Mg_2$ = 14.09% P_2O_5.
0.6472 gram gave 0.3900 gram gold = 67.63%.

Here the ratios are 9 Au_2O_3 : 6 P_2O_5 : 4 BaO.

In the silver salt (Patterson) :

0.7718 gram 0.0915 gram AgCl = 9.58% Ag_2O.
0.7718 gram 0.4470 gram gold = 64.98%.
0.7718 gram 0.1584 gram $P_2O_7Mg_2$ = 13.13% P_2O_5.

The ratios are approximately 16 Au_2O_3 : 10 P_2O_5 : 5 Ag_2O.

The analyses of the barium and silver salts are at least sufficient to show that no simple double decomposition takes place in either case. The formula which I have given for the gold salt is to be regarded as purely empirical, and does not explain the explosive character of the salt. No compounds falling under the general expression $Au_2(NH_3)nO_3$ are at present known. Dumas and Raschig give to fulminating gold the formula $NH_2 . Au''' . NH$, which may be written N_2H_3Au'''. This is equivalent to 2 NH_3; the corresponding ammonium must be $N_2H_3Au'''H_2$, and the oxide of this $(N_2H_5Au''')O$. If we assume that this oxide is present in the auramin pyrophosphate which I have described, we may write the formula

$$8\,Au_2O_3 \,.\, 6\,P_2O_7Au'''Na \,.\, 6\,\{(N_2H_5Au''')O\}\,(NH_4)_2O \,.\, 2H_2O + 24\text{ aq.},$$

which is reducible to the type

$$8\,R_2O_3 \,.\, 7\,RO + 6\,P_2O_7R'_4 + 26\text{ aq.}$$

As regards the deduction of the formula from the analyses, it may be worth while to give also the equations

$$6\,P_2O_5 + 3\,Au_2O_3 + 3\,Na_2O = 6\,P_2O_7Au'''N\,;$$
$$3\,Au_2O_3 + 12\,NH_3 = 6\,\{(N_2H_5Au''')O\} + 3\,H_2O.$$

In the determination of the ammonia by boiling with KHO or NaHO, we have

$$6\,N_2H_5Au''' + 3\,H_2O = 12\,NH_3 + 3\,Au_2O_3.$$

Auro-pyrophospho-Molybdates.

When a solution of chloro-aurate of sodium, $AuCl_4Na$, is mixed with one of pyrophospho-molybdate of sodium, a dull orange-colored fine-grained crystalline precipitate is thrown down, which is almost certainly an auro-pyrophospho-molybdate of sodium. When a solution of auro-pyrophosphate of sodium, P_2O_7AuNa, is boiled for some time with 14 : 6 molybdate of ammonium, a pale buff-colored crystalline precipitate is formed, which is slightly soluble in boiling water, giving however only a turbid liquid. After washing with cold water this precipitate was dried *in pleno* over sulphuric acid. Of this salt:

0.5581 gram lost by ignition with WO_4Na_2 0.0841 gram = 15.07% $H_2O + NH_3 + O$.

$$\left\{\begin{array}{l}\text{0.8123 gram gave 0.3489 gram gold} = 42.94\% = 48.18\%\ Au_2O_3.\\ \text{0.8123 gram gave 0.0837 gram } P_2O_7Mg_2 = 6.59\%\ P_2O_5.\end{array}\right.$$

0.6133 gram gave 0.2615 gram gold = 42.13% = 47.85%.

0.2746 gram gave 0.01558 gram NH_3 = 5.65% NH_3.

0.4774 gram lost by ignition with WO_4Na_2 0.0744 gram = 15.58%.

In this last analysis the salt had probably absorbed a little water. The same is true for the next:

0.6133 gram gave 0.0624 gram $P_2O_7Mg_2$ = 6.51%.

If we calculate the analyses for an anhydrous salt, we find:

		Calculated.	Found.	
11 MoO_3	1584	36.07		
5 Au_2O_3	2206	50.25	50.29	50.27
2 P_2O_5	284	6.46	6.87	6.83
15 NH_3	255	5.81	5.89	
Na_2O	62	1.41		
	4391	100.00		

In the hydrated salt the ratios are nearly

$$11\ MoO_3 \,.\, 5\ Au_2O_3 \,.\, 2\ P_2O_5 \,.\, 15\ NH_3 \,.\, Na_2O + 10\ aq.$$

The formula requires 3.93% of water. The mean of the water in the two analyses is 4.18. It is to be borne in mind that the salt could not be recrystallized, and was probably not absolutely pure. The salt does not explode on heating, but merely "puffs." Hot dilute chlorhydric acid readily dissolves it. Ammonia water does not sensibly dissolve it, but gives an orange-colored substance which may be the corresponding auramin compound. The formula may be written provisionally

$$22\ MoO_3 \,.\, 4\ P_2O_7Au'''Na \,.\, 6\ Au_2O_3 \,.\, 15\ (NH_4)_2O + 5\ aq.$$

More extended investigations are necessary to fix the formulas of this and analogous compounds. Analysis by Mr. G. W. Patterson.

Auramin-pyrophospho-Molybdates.

When the orange-colored flocky precipitate formed by adding ammonia to auro-pyrophosphate of sodium is boiled for some time with 14 : 6 ammonic molybdate, and the whole allowed to stand with the supernatant liquid, a pale yellowish crystalline salt is formed. After thorough washing with cold water, the salt was dried on bibulous paper and *in pleno* over sulphuric acid. For analysis it was boiled for a short time with a mixture of chlorhydric and sulphurous acids. The phosphoric acid was determined in the filtrate from the gold by magnesia mixture, in the manner which I have pointed out in treating of the analysis of the phospho-molybdates.* The filtrate from the ammonio-magnesic phosphate, after adding $(NH_4)_2S$, was evaporated, filtered to separate free sulphur, and then treated with cold dilute chlorhydric acid. The precipitated MoS_3 was filtered on a Gooch filter, washed, dried at 106° C., then washed several times with carbon disulphide, dried, and weighed. Ammonia was determined by boiling with sodic hydrate and titration.

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* Proceedings of the American Academy, XXIX. 64.

(1) 0.3969 gram gave 0.0217 gram NH_3 = 5.47%.
(2) 0.5733 gram gave 0.3612 gram gold = 70.68%.
(3) 0.5733 gram gave 0.1168 gram $P_2O_7Mg_2$ = 13.03% P_2O_5.
(4) 0.5733 gram gave 0.0426 gram MoS_3 = 5.57% MoO_3.
(5) 0.3499 gram lost on ignition with WO_4Na_2 0.0703 gram = 20.09%.

The salt explodes on heating, but not violently. There appears to have been a slight loss on heating with sodic tungstate, and I have accordingly calculated the water by difference, all the other constituents having been determined directly. The analyses correspond to the formula 12 $Au_2O_3 \cdot 3\,MoO_3 \cdot 7\,P_2O_5 \cdot 24\,NH_3 + 21$ aq. Analysis by Mr. G. W. Patterson:

		Calculated.	Found.
12 Au_2O_3	5297	70.54	70.68
3 MoO_3	432	5.75	5.57
7 P_2O_5	994	13.23	13.03
24 NH_3	408	5.44	5.47
21 H_2O	378	5.04	5.25
	7509	100.00	

Here, as in the cases of the other gold compounds, part of the ammonia is present as ammonic oxide and part is directly combined with gold; but the proportions remain to be determined. The careful study of this class of compounds appears likely to lead to very interesting results. I have classed them only provisionally with complex acids.

As it may not be possible for me to return to the subject,* I will here give the results of some preliminary work, which will at least serve as starting points for further investigation.

Molybdico-Tungstates.

When acid molybdate of ammonium is boiled with chlorhydric acid and potassic iodide, and the deep orange-colored liquid is precipitated with ammonia, a brown precipitate of $Mo(OH)_4$ is thrown down, which after thorough washing is readily soluble in a solution of 12 : 5 sodic tungstate, forming a deep orange-red liquid. Potassic bromide gives a buff-colored crystalline precipitate, which is soluble in boiling water, and crystallizes on cooling in small pale brown scales. Ammonic chloride gives a similar salt, as do also the chlorides of barium, strontium, and calcium. All these salts are soluble in hot water, and separate from the solution in pale brown crystals. In preparing the potassium salt a large excess of potassic bromide should be used: the bromide in this, as in many other cases, appears to be preferable to the chloride and nitrate. In these salts the molybdic dioxide may be easily and accurately determined by titration with permanganate, after adding sulphuric acid. The solutions of the molybdico-tungstates readily absorb oxygen from the air, forming molybdic teroxide, a fact which must be taken into account in analysis.

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* "A rebus gerendis senectus abstrahit." — Cicero, *Cato Major.*

Molybdic hydrate, $Mo(OH)_4$, quickly reduces MoO_3 in a solution of 14 : 6 ammonium salt, and gives a fine blue liquid, which probably contains Mo_2O_5 or $MoO_2 + MoO_3$. When a very cold solution of ammonic molybdate is employed, and molybdic hydrate is added in small portions at a time, the solution becomes yellow, then quickly green, and finally blue. It is possible that a molybdico-molybdate, $m MoO_2 . n MoO_3 . p R_2O$, is formed at first. Molybdic hydrate reduces both molybdic and tungstic teroxides in phospho-molybdates and phospho-tungstates. Analyses of the potassium, calcium, and barium molybdico-tungstates were made with salts which perhaps were not absolutely pure. The formulas obtained appeared to be respectively $12\,WO_3 . MoO_2 . 5\,K_2O + 16$ aq.; $12\,WO_3 . MoO_2 . 5\,CaO + 32$ aq.; and $12\,WO_3 . MoO_2 . 6\,BaO + 30$ aq.; but these are given with much reserve. In these the molybdenum was determined by titration with permanganate, and the sum of the molybdic and tungstic teroxides, after oxidation, by precipitation of the neutral solution with calcic or baric chloride. Tungstic teroxide could then be determined by difference.

It seems at least probable that tungstico-molybdates corresponding to molybdico-tungstates, as, for example, $12\,MoO_3 . WO_2 . x RO$, also exist.

Uranoso-Tungstates.

When uranic oxide is dissolved in dilute sulphuric acid, and the solution is treated with metallic zinc, a solution of sulphate of uranic dioxide is formed which after a time deposits a gray-green powder insoluble in cold water, and probably a basic sulphate. This body treated with a solution of 12 : 5 sodic tungstate gives at once an olive-green crystalline salt very insoluble in hot water. The supernatant liquid has a peculiar reddish tint. The dark olive-green salt is oxidized by boiling with nitric acid and gives a yellowish white mixture, or possibly compound, of uranic and tungstic teroxides, easily decomposed by boiling with caustic alkalies, with separation of uranic oxide and formation of sodic tungstate. A solution of 12 : 5 potassic tungstate acts in the same manner upon the uranious salt, giving also an olive-green crystalline salt and a brown-red solution. Similar results were obtained with acid ammonic tungstate. After drying for some days upon paper, the sodium salt was analyzed by Dr. Loeb:

0.4436 gram lost with WO_4NO_2 0.0331 gram = 7.46%.
0.9861 gram gave 0.3954 gram WO_3 = 40.09%.
0.9861 gram gave 0.3360 gram UO_2 and $KMnO_4$ = 34.08%.

The analyses lead to this formula,

$$8\,WO_3\,.\,6\,UO_2\,.\,12\,Na_2O + 25\,aq.$$

		Calculated.		Found.	
8 WO_3	1856	39.69	74.46	40.09	74.17
6 UO_2	1626	34.77		34.08	
12 Na_2O	744	15.92		16.46 (diff.)	
25 H_2O	450	9.62		9.47	
	4676	100.00			

The water determination was made by heating with sodic tungstate and determining the loss of weight. In the fusion the UO_2 is completely reoxidized to UO_3. Hence a correction must be applied to the water, which in the above case amounts to 2.01% to be added. As the salt could not be recrystallized, it was doubtless not perfectly pure.

The olive-green potassium salt is also insoluble in hot water and in chlorhydric acid. It reduces silver and mercury from their nitrates, and appears to undergo double decomposition with baric and calcic chlorides. This salt was also analyzed by Dr. Loeb:

1.3260 grams gave 0.4997 gram WO_3 = 37.69%.
1.3260 grams gave with $KMnO_4$ gram UO_2 = 33.21%.
0.9275 gram lost on ignition with WO_4Na_2 0.0833 gram = 8.98%.

The analyses lead to the formula,

$$8\,WO_3\,.\,6\,UO_2\,.\,9\,K_2O + 34\,aq.$$

		Calculated.		Found.	
8 WO_3	1856	37.58	70.50	37.69	70.90
6 UO_2	1626	32.92		33.21	
9 K_2O	846	17.12		16.60 (diff.)	
34 H_2O	612	12.38		12.50	
	4940	100.00			

The potassic salt corresponds in constitution to the sodic salt if we write it:

$$8\,WO_3\,.\,6\,UO_2\,.\,9\,K_2O\,.\,3\,H_2O + 31\,aq.$$

Silico-Molybdates.

The existence of definite silico-molybdates appears to have been first observed by Parmentier,* who obtained potassium, sodium, and ammonium salts by the action of alkaline silicates upon alkaline molybdates in presence of nitric acid. The free acid has the formula $12\ MoO_3\ .\ SiO_2 + 26\,aq.$ I have devised another method of preparing this class of salts, which may perhaps be generalized in its application. When a solution of fluosilicic acid is poured into one of 14 : 6 molybdate of ammonium, no precipitate is formed, but the solution becomes yellow. On evaporation a bright yellow crystalline body separates in large quantity. When normal sodic molybdate, MoO_4Na_2, is strongly acidulated with chlorhydric acid, the addition of fluosilicic acid gives at once a bright yellow color. The solution obtained in this manner gives no precipitate in the cold with ammonic chloride, but on boiling and shaking for a few minutes a beautiful bright yellow crystalline precipitate is thrown down in abundance. This is slightly soluble in hot water to a yellow liquid. A solution of fluosilicic acid mixed with one of an acid potassic molybdate forms no precipitate, but the mixture is yellow, and on evaporation to dryness upon a water bath yields a highly crystalline yellow powder. Much molybdic teroxide is at the same time reduced to blue oxide. The yellow solutions of the silico-molybdates of potassium and sodium give with nitrate of croceocobalt a beautiful orange crystalline precipitate, which is insoluble in cold water and readily washed and dried. The bright yellow silicomolybdate of ammonium after careful washing was analyzed:

0.7963 gram lost on ignition with WO_4Na_2 0.0750 gram NH_3 and $H_2O = 9.42\%$.
0.5279 gram left on ignition 0.0158 gram $SiO_2 = 2.99\%$.
0.6504 gram gave 0.0339 gram $(NH_4)_2O = 5.22\%$.
0.5817 gram gave 0.03045 gram $(NH_4)_2O = 5.23\%$.

The analyses correspond to the formula,

$$12\ MoO_3\ .\ SiO_2\ .\ 2\ (MH_4)_2O + 5\ aq.\,;$$

which requires:

		Calculated.	Found.	
$12\ MoO_3$	1728	87.18	87.58 (diff.)	
SiO_2	60	3.03	3.00	
$2\ (NH_4)_2O$	104	5.24	5.22	5.23
$5\ H_2O$	90	4.55	4.20	
	1982	100.00		

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* Comptes Rendus, XCII. 1234, and XCIV. 213.

The silica was determined by igniting the salt with free access of air until all the molybdic oxide was expelled. The reactions of a solution of the sodium salt were as follows. No precipitate with baric and calcic chlorides. None at first with potassic bromide, but on standing bright yellow crystals formed. A sulphur yellow crystalline precipitate with mercuric nitrate and a beautiful bright orange-yellow highly crystalline precipitate with mercurous nitrate. A very pale yellow crystalline precipitate with argentic nitrate and a pale yellow fine-grained crystalline precipitate with thallous nitrate. Pechard * has obtained the same salt by precisely the same process as that which I have employed, and has priority in publication. I have also obtained a titanio-molybdate and a zirconio-molybdate by similar methods, but have not analyzed them. Pechard has described beautiful salts of the two series, and rendered further work on my part unnecessary.

Selenoso-Molybdates.

When 24 : 1 phospho-molybdate of potassium is boiled with a solution of potassic selenite SO_3K_2 it readily dissolves to a perfectly clear and colorless liquid, which after an hour deposits beautiful large granular colorless crystals in abundance. These are readily soluble in hot water, and crystallize from the solution without change, except that large transparent colorless crusts are obtained. Of this salt, analyzed by Mr. G. W. Patterson:

$\{$ 1.1360 grams gave 0.1503 gram of selenium = 13.23% = 18.09% SeO_2.
$\{$ 1.1360 grams gave 0.7772 gram $PtCl_6K_2$ = 13.27% K_2O.
0.9570 gram lost up to 175° C. 0.0058 gram H_2O = 0.61%.

Deducting the small percentage of water, the analyses correspond to the formula.

$$17\ MoO_3\ .\ 6\ SeO_2\ .\ 5\ K_2O.$$

		Calculated.	Found.
17 MoO_3	2448	68.81	68.45
6 SeO_2	648	18.16	18.20
5 K_2O	472	13.23	13.35
	3568	100.00	

The formula may also be written,

$$6\ \{SeO_2\ .\ 2\ MoO_3\} + 5\ MoO_4K_2.$$

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* Comptes Rendus, CXVII. 691–694. Cited in Zeitschift für anorg Chemie, VI. 200.

The selenium was determined by reduction with sulphurous acid and the molybdic oxide by difference. In spite of the mode of preparation, the salt did not contain phosphoric pentoxide. On repeating the preparation of the salt I obtained different results, the proportions used being probably not the same. The solution deposited first groups of colorless crystals, and then gave after further evaporation a white granular crystalline salt. The grouped crystals seemed at first to be quite insoluble in water, but when boiled dissolved, and then crystallized out very readily. Perhaps more than one salt was formed in this operation. The solution of the salt analyzed gave pale yellow crystalline precipitate with argentic and mercurous nitrates.

Selenoso-Tungstates.

When ammonic tungstate is boiled with a solution of SeO_3H_2 it readily dissolves to a pale yellow solution, which almost immediately gives beautiful shimmering scales in a pale yellow mother liquor. These pass at once through a filter and are difficult to separate and wash. Potassic tungstate also readily dissolves in a solution of selenious acid, forming a pale yellow solution which on heating suddenly becomes opaque, while a pale yellow precipitate is thrown down. When washed by decantation with cold water, both the ammonic and potassic salts have a distinct pale yellow color. When a solution of selenious acid is mixed with one of 12 : 5 sodic tungstate and a solution of potassic bromide is added, a white precipitate in very minute granular crystals is formed, settling rather slowly, and very slightly soluble in hot water. A solution of argentic nitrate gave, with the well washed salt, large very pale yellow crystalline flakes. Mercurous nitrate gave a pale yellow crystalline precipitate. A solution of selenious acid mixed with one of 24 : 1 : 2 sodic phospho-tungstate gave a white granular precipitate very slightly soluble in hot water. After careful washing, this gave, on boiling with argentic nitrate, a perfectly white crystalline salt, a bright yellow crystalline precipitate with mercurous nitrate, and a white crystalline precipitate with baric chloride. It is possible that phospho-selenoso-tungstates are formed in this manner.

Pechard * has recently described salts of two series of molybdo-selenites, as he terms them, having respectively formulas which would indicate that they are derivatives of the acids:

$$4\,H_2O\,.\,3\,SeO_2\,.\,10\,MoO_3, \quad \text{and} \quad 2\,H_2O\,.\,SeO_2\,.\,5\,MoO_3.$$

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* Comptes Rendus, CXVI. 1441-1444; also, CXVII. 104-106.

The same chemist has also described a very interesting series of salts, which he terms molybdo-sulphites, embraced under the general formula,

$$4\,H_2O\ .\ 3\,SO_2\ .\ 10\,MoO_3.$$

Telluroso-Molybdates and Tungstates.

Klein * many years since also observed the existence of complex acids containing tellurous and telluric oxides and tungstic oxide. So far as I am aware, no analyses have been published. A preliminary notice of my own work was communicated to the Harvard Chemical Club, February 12, 1884.†

When a solution of $TeBr_6K_2$ is formed with a large excess of water, the salt is completely decomposed into bromhydric and tellurous acid TeO_3H_2. A solution of 14 : 6 acid molybdate of ammonium readily dissolves this last on boiling, and the clear filtered solution soon deposits beautiful granular colorless crystals in quantity. It is best to use an excess of tellurous acid. The telluroso-molybdate is much less soluble than the acid molybdate of ammonium, and may be redissolved and recrystallized without apparent decomposition. When a solution of the $TeBr_6K_2$ is mixed with one of the acid molybdate, a very pale yellow precipitate is formed. After standing, small bright yellow crystals also appear. The white precipitate is probably only tellurous acid. When freshly precipitated tellurous acid is boiled with a strong solution of an acid potassic tungstate, it does not dissolve, but changes character and becomes more distinctly crystalline. A solution of $TeBr_6K_2$ gives with one of 24 : 1 : 2 phospho-tungstate of sodium a very white granular precipitate, which is insoluble, and may be washed with boiling, but then settles slowly. The tellurium employed was the best commercial product, and doubtless not absolutely pure. If, as has been supposed, two different metals are embraced under the name, it is possible that the compounds of the two oxides with molybdic and tungstic oxides may afford means of separation in consequence of differences in composition and properties. Should tellurium be hereafter found to possess a technical value or interest, an abundant supply can be furnished by the mines of Colorado. The very high cost of the metal at present has prevented further study on my part.

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* Bull. de la Société Chimique, [2.], XLII. 169.

† See also Berichte der deutschen chem. Gesellschaft, XVIII. 1089. August, 1884.

Cerico-Molybdates.

When ceric fluoride, CeF_4, is boiled in a platinum dish with 14 : 6 molybdate of ammonium, the solution quickly becomes yellow, and soon deposits a fine yellow crystalline salt, which may be washed with cold water, in which it is but slightly soluble. It contains molybdic teroxide, ceric oxide, and ammonia. Basic ceric nitrate treated with a solution of hydro-potassic fluoride, KF_2H, changes character at once and becomes flocky-crystalline. After washing with cold water, boiling with 14 : 6 molybdate of ammonium dissolves but little, but the salt becomes bright sulphur-yellow and crystalline and is practically insoluble in water. The best method of preparing this salt consists in first preparing pure basic nitrate of cerium[*] free from lanthanum and didymium (neo-dymium and praseo-dymium). This is to be dissolved in nitric acid and the solution diluted. Acid potassic fluoride then precipitates a nearly white flocky salt, which dissolves readily in a boiling solution of 14 : 6 molybdate of ammonium to a yellow solution, and crystallizes from this. It will probably be better to boil with a solution of an acid sodic molybdate, as this yields a soluble sodic salt, the solution of which gives with ammonic chloride a yellow crystalline precipitate of an ammonium salt, which will make a good starting point for further investigations.

When the ceric fluorine salt, prepared as above with KF_2H, is boiled with 10 : 4 sodic tungstate, a fine bright yellow solution is formed which gives a beautiful orange crystalline precipitate with nitrate of croceo-cobalt. In preparing the fluorine compound it is best to add a cold filtered solution of KF_2H to the basic ceric nitrate diffused in cold water, and not to heat at all. Ceric hydrate dissolves with difficulty in solutions of acid tungstates and molybdates, more easily when precipitated from cold solutions.

NOTE ON CERTAIN TUNGSTATES, AND ON A NEW PHOSPHO-TUNGSTATE.

In other instalments of my work I have endeavored to show[†] that there exists a special class of metatungstates, of which the lowest term has the general formula $4\,WO_3 . RO$, and the highest the general formula $24\,WO_3 . 11\,R_2O$. This view appeared to be supported both by my own work and by that of Marignac, but has not found favor with chemists, and has in fact, so far as I am aware, passed wholly unnoticed. The highest term actually obtained by me* appeared to have the formula:

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[*] See my paper in American Journal of Science, XXXVII. 352.

[†] Proceedings of the American Academy, XV. 15.

$$16\,WO_3 \,.\, 3\,Na_2O \,.\, 4\,(NH_4)_2O + 18\text{ aq.}$$

The only complete analysis made agreed well with this formula, and differed very materially from that of the 12 : 5 ammonia-sodic tungstate. As it has been asserted, however, that the two are identical, Mr. Charles D. Smith has made in my laboratory four analyses with portions of the salt which had been preserved. The analyses are as follows:

0.7226 gram gave 0.6038 gram = 83.55% WO_3.
1.1598 grams gave 0.9687 gram = 83.54% WO_3.
1.3281 grams gave 1.1091 grams = 83.51% WO_3.
1.4740 grams gave 1.2309 grams = 83.50% WO_3.
1.2726 grams gave 0.0604 gram $(NH_4)_2O$ = 4.75%.
1.0901 grams gave 0.0508 gram $(NH_4)_2O$ = 4.66%.
1.1360 grams gave 0.0532 gram $(NH_4)_2O$ = 4.67%.
0.6756 gram gave 0.0318 gram $(NH_4)_2O$ = 4.72%.
4.4687 grams lost on ignition 0.5292 gram = 11.84% NH_3 and H_2O.
3.0697 grams lost on ignition 0.3638 gram = 11.84% NH_3 and H_2O.
4.6030 grams lost on ignition 0.5444 gram = 11.82% NH_3 and H_2O.
3.3885 grams lost on ignition 0.4014 gram = 11.84% NH_3 and H_2O.

The analyses correspond to the formula,

$$24\,WO_3 \,.\, 5\,Na_2O \,.\, 6\,(NH_4)_2O + 27\text{ aq.},$$

which requires:

		Calculated.	Mean.	I.	II.	III.	IV.
24 WO_3	5568	83.40	83.52	83.55	83.54	83.51	83.50
6 $(NH_4)_2O$	310	4.68	4.70	4.75	4.66	4.67	4.72
5 Na_2O	312	4.65	4.65	—	—	—	—
27 H_2O	486	7.27	7.13	7.08	7.14	7.16	7.11
	6676	100.00					

The sodic oxide is determined by difference. The analyses agree rather more closely with the new formula than with that formerly given, which I will cite for the sake of comparison:

$$16\,WO_3 \,.\, 4\,(NH_4)_2O \,.\, 3\,Na_2O + 18\text{ aq.},$$

requires:

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* Ibid., XVI. 76.

		Calculated.	Found.
16 WO_3	3712	83.77	83.94
4 $(NH_4)_2O$	208	4.69	4.64
3 Na_2O	186	4.20	4.21
18 H_2O	324	7.32	7.21
	4430	100.00	

It is certainly difficult to decide between these two formulas, only it must be observed that the higher formula is derived from the mean of four analyses, which agree well with each other, and has therefore the weight of analytical evidence in its favor until further research shall prove its inaccuracy. Still another formula has been proposed by Von Knorre,* who writes $12\ WO_3 . 3\ (NH_4)_2 . 2\ Na_2O + 13$ aq., which requires 84.41% WO_3, 4.73% $(NH_4)_2O$, 3.76% Na_2O, and 7.10% H_2O. The correspondence between the results of the analyses and the data required by the formula is much less than with the formula which I first gave and which Von Knorre rejects, and of course still less than with the new formula.

New Phospho-Tungstate.

Pure normal sodic tungstate was mixed in solution with sodic orthophosphate, $PO_4Na_2H + 12$ aq., in the proportion of twelve molecules of the first to one of the second salt, and chlorhydric acid added in small excess. A phospho-tungstate crystallized from the solution, and was redissolved and twice recrystallized. The new salt was in fine colorless crystals, less soluble than the now well known salt which has the formula, $24\ WO_3 . P_2O_5 . 2\ Na_2O + 27$ aq. The salt was dried on paper for analysis. It effloresced or became opaque in dry air. Mr. Charles D. Howard obtained the following results on analysis.

1.4941 grams lost on ignition with WO_4Na_2 0.1078 gram = 7.21% H_2O.
1.4502 grams lost on ignition with WO_4Na_2 0.1046 gram = 7.21% H_2O.
1.0950 grams gave 1.0019 grams $WO_3 + P_2O_5$ = 91.49%.
1.1950 grams gave 1.0975 grams $WO_3 + P_2O_5$ = 91.58%.
1.6782 grams gave 0.0720 gram $WO_3 + P_2O_5$ = 2.74% P_2O_5.

The analyses lead to the formula,

$$20\ WO_3 . P_2O_5 . Na_2O . 2\ H_2O + 19\ \text{aq.},$$

which requires:

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* Berichte der deutschen chem. Gesellschaft, XIX. 823.

		Calculated.	I.	II.
20 WO_3	4640	88.85	88.75	88.84
P_2O_5	142	2.73	2.74	
Na_2O	62	1.18	1.25	
21 H_2O	378	7.24	7.21	7.21
	5222	100.00		

The only 20 : 1 phospho-tungstate which I have hitherto described * contained 6 molecules of base (BaO), and perhaps the new salt should be written $20\,WO_3 . P_2O_5 . Na_2O . 5\,H_2O + 16$ aq. With respect to its formation with the proportions given, I may remark that I have in repeated trials failed to obtain the salt

$$24\,WO_3 . P_2O_5 . 2\,Na_2O + 27 \text{ aq.}$$

by mixing sodic tungstate and phosphate in the exact theoretical proportions and adding chlorhydric acid to the mixed solutions. The quantity of phosphate necessary to be added is much more than one molecule for twelve molecules of the tungstate. This remark appears to have been made by other chemists also.

Kehrmann † has recently described phospho-tungstates which come under the general formula $18\,WO_3 . P_2O_5 . 3\,RO$, the salts being

$18\,WO_3 . P_2O_5 . 3\,K_2O + 14$ aq., and $18\,WO_3 . P_2O_5 . 3\,(NH_4)O + 14$ aq.

He gives to the acid the name "Phospholuteo-wolframsäure"; but though there is little doubt that there is here a hitherto undescribed series, the analyses are not satisfactory.

In another part of this paper I have described three salts of a phosphotungstic acid which would have the formula,

$$18\,WO_3 . P_2O_5 . 6\,H_2O,$$

the salts themselves having respectively the formulas,

$18\,WO_3 . P_2O_5 . 6\,K_2O + 23$ aq.; $18\,WO_3 . P_2O_5 . 6\,K_2O + 30$ aq.:

and $18\,WO_3 . P_2O_5 . K_2O . 5\,H_2O + 14$ aq.

These salts are however colorless, and if we admit the accuracy of Kehrmann's formulas, there must be two isomeric series. Kehrmann appears to have been wholly unacquainted with my work.

Experiments to determine the relations of WS_4K_2, MoS_4K_2, and $WS_2O_2K_2$, to phosphates and arsenates have not led to definite results,

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* Proceedings of the American Academy, XVI. 127, and Am. Chemical Journal, II. 282.

† Zeitschrift für anorganische Chemie, IV. 138, 386.

though there seemed to be a relation of some kind. The same statement applies to the various oxyfluorides of molybdenum and tungsten.

In a communication made to the British Association * at the Montreal meeting, in 1884, I stated that complex acids existed into which platinum chloride entered, as, for instance, compounds of the type $2\ PtCl_2 . R_2O_3$. Since then I have made various communications on the same subject to the Harvard Chemical Club. I regard these compounds as respectively phosphoric, arsenic, and antimonic oxides, in which $2\ PtCl_2$ replaces O_2. A great amount of work on the subject has been done, but as it is at least possible that a very different view of the subject may be taken, I will reserve the results of my work for another occasion.

NEWPORT, R. I., August 1, 1894.

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* Report for 1884, p. 670.

(To be continued.)

XII.

CONTRIBUTIONS FROM THE ZOÖLOGICAL LABORATORY OF THE MUSEUM OF COMPARATIVE ZOÖLOGY, UNDER THE DIRECTION OF E. L. MARK, XLIII.

ON THE BLASTODERMIC VESICLE OF SUS SCROFA DOMESTICUS.

By A. W. Weysse.

Communicated by E. L. Mark. Received August 10, 1894.

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I. Introduction.

1. *Subject.*

In the latter part of the summer of 1893 the opportunity was opened to me of obtaining young embryos of Sus scrofa domesticus. So I let the work rest which I had in hand on the development of some other mammals and began investigations on this. I was fortunate enough to secure a number of embryos several days younger than the youngest of the six, from fourteen to fifteen days old, which Keibel ('93) has recently described so elaborately; and since these present phenomena of development unusual in the ontogeny of the Mammalia, it has seemed best to record them, in the hope that they may possibly lead to similar discoveries in allied forms.

The incompleteness of our knowledge of the early stages in the embryology of the higher viviparous animals is due largely, of course, to the difficulty of securing sufficient material in successive stages of growth, and there is the further difficulty that it is impossible to determine in the great majority of cases the exact age of the embryos, since spermatozoa may remain for several hours, days, or even months, within the body of the female before fertilization takes place. And further, it has long been known that, especially during the earlier phases of development, ova which were apparently fertilized at the same time grow at very different rates, so that within one uterus we may find embryos illustrating several stages of ontogeny. For these reasons I cannot give exact ages for the embryos I am about to describe, though in almost every case I can give the period which has elapsed between coitus and the time when the sows were killed and the embryos obtained.

2. *Material.*

The present paper is based on the results obtained by the study of thirty embryos taken from four sows. In all I had nine sows served at different times, and these were killed at from nine to eleven days after coitus. Only three of the nine proved to be pregnant at the time they were killed, and of these three, two were killed ten days and the other eleven days after copulation. Each of the two sows killed on the tenth day contained eleven embryos in varying stages of development, though all the embryos in one were much less advanced than those in the other, as I conclude from the difference in the size both of the embryos and of the cells of which they are composed, and from the difference in the size and structure of the germinal disks. The third sow, killed on the eleventh day, contained only four embryos, two of which were as old as the oldest of those from the first two sows; the other two were younger. The remaining four embryos of the thirty were found in a sow which had been served before coming under my control, and were apparently in about the same stage ontogenetically as some of the older embryos in the first two cases mentioned above. The uterus in which these last embryos lay, contained six in all, but two were so badly folded as to be unavailable as far as the study of the germinal disk was concerned. These embryos were obtained by opening a large number of apparently empty uteri; in this way I have found about 3% of the individuals examined pregnant, but all of the embryos with the exception of the six just mentioned were in a much more advanced stage of devolopment, so that they afford no information on the subject matter of the present article, and I shall reserve the consideration of them for a future paper.

3. *Technique.*

In the case of the first uteri which I opened, I followed with some variations one of the methods which Keibel ('93) has described in his work on the pig. When the uterus had been removed from the animal, it was cut open along the side opposite the mesometrium and placed in a flat-bottomed glass dish containing Kleinenberg's picro-sulphuric mixture and resting on a black tile. Then, by carefully spreading out the complicated folds of the inner wall of the uterus and gently agitating them, the embryos readily floated out into the fluid, and could be distinguished at once against the black surface of the tile. They were then carefully removed on a spatula to a smaller vessel of the picro-sulphuric mixture, where they remained several hours and were then transferred to 70% alcohol, and after twelve or fourteen hours to 90% alcohol, which was gently warmed and changed several times until all trace of the acid had been washed out. But this method had some minor disadvantages which seemed avoidable; the action of the acid mixture on the instruments used, and the staining of the hands, were at least undesirable, and to be avoided unless absolutely necessary. Accordingly, in my later work, instead of using Kleinenberg's mixture as a medium for floating out the embryos from the uterus, I employed normal salt solution (0.75% NaCl in water), at a temperature of about 40° C. Keibel ('93) says that he did not use this because it is said to injure the embryos, and Bonnet ('84) found that, if embryos lay a long time in this solution, they became swollen. This is doubtless true, if they remain in the fluid as long as is necessary to detach such complicated embryos as Keibel worked with, some of which were more than a meter long and greatly folded amongst the plications of the uterine wall. The same may be true for the embryos of the sheep, — upon which Bonnet worked, — which at a corresponding stage of development closely resemble those of the pig, but in the case of such small embryos as those which I have been concerned with the very short time during which it is necessary for them to remain in the salt solution has absolutely no effect either on the general form of the embryo or on the histological conditions, as my sections clearly demonstrate. As soon as the embryos were floated out from the uterus, they were at once transferred as before to Kleinenberg's picro-sulphuric mixture. All the embryos which I have studied have been fixed in this fluid. Had my supply of material been larger, I should have employed several other fixing reagents, but my work on young embryos of other mammals, as well as the results of the experiments of other embryologists, gave me complete confidence in the reliability of this reagent for the material in hand. The results in this case were in the highest degree satisfactory.

After the specimens had been entirely freed from acid, drawings of them as opaque objects seen against a black background were made with the aid of an Abbé camera lucida; they were then returned to 70% alcohol, and from this transferred to Kleinenberg's alcoholic hæmatoxylin (70%) diluted with twice its volume of his solution of calcium chloride and alum. Here they remained for a few hours, the time varying according to the size of the embryos, and were then transferred to a 0.1% solution of hydrochloric acid in 70% alcohol, the process of decolorizing being carefully watched under the microscope until the object had attained the proper color. It was then placed in 70% alcohol containing a slight trace of ammonia, which made the stain permanent by neutralizing the acid. I have found that washing simply in neutral alcohol, though it be never so carefully done, will not always prevent an ultimate fading of this stain; the addition of ammonia is an absolute essential if one wishes to be perfectly sure that the sections will not fade. Objects which I have treated thus have always preserved their color. In my work on the pig I have not as yet used carmine stains. On the embryos of both the rat and the mouse I have obtained very brilliant results, both with borax carmine and with hydrochloric carmine, but, so far as I could see, they had no advantage over hæmatoxylin. The last is valuable because of its high alcoholic grade, and because, when properly decolorized, it becomes a most highly differential stain for these embryonic tissues. Small semi-transparent objects, like the embryos of the pig at this stage of development, can readily be decolorized *in toto*, for the extent of the decolorizing can be determined by the aid of the microscope; but opaque objects, like the uterus of the mouse, have to be decolorized largely after sectioning.

When the embryos had been stained and decolorized, they were cleared in chloroform, embedded in paraffine, and cut on the Minot-Zimmerman microtome into sections 10 μ thick. They were then spread on the surface of distilled water, which rested on a thin film of albumen affixative covering the slide. The slide was gently warmed in an alcohol flame, until the sections became perfectly smooth. Finally the water was removed, the paraffine dissolved out in xylol, and the sections mounted in Canada balsam.

I have given this rather extended account of my technique in order to show that there has been no lack of care in this direction which could affect the histological condition of my specimens. I will now give a description of the embryos themselves, and then proceed to a consideration of the investigations of other authors, and to the theoretical interpretation of the phenomena described.

II. Description of the Embryos.

1. *General Characteristics of the Blastodermic Vesicle.*

The embryos are all in more or less advanced stages of the so-called blastodermic vesicle or didermic blastocyst, as it has been described by Balfour ('81), Van Beneden ('80), Hubrecht ('90), Bonnet ('91), and others. They consist in general of at least two well defined layers, — an outer of more or less isodiametric cells, and an inner, in contact with the outer, of greatly flattened cells, which are very much larger than those of the outer layer. There is no trace of cells lying between these two layers at any point. At one region of the embryo, the outer layer of cells is thickened, forming the germinal disk. For the sake of convenience this region may be spoken of as the germinal or embryonic area, and the rest of the vesicle as the extra-germinal or extra-embryonic region. In most cases there is evidence of a third layer of cells, which is outside the two layers just mentioned, and is in a more or less disintegrated condition. I shall later refer to this more at length.

It has not seemed to me necessary to give figures of the whole blastocyst. In each case it consists of a hollow vesicle with a double wall, which if fully distended would be about spherical. I have never found the vesicles completely distended, and often they are greatly folded, so that it is not always possible to make sections in just the plane one wishes; for if the germinal disk lies on the edge of a fold, it is usually necessary to cut at right angles to the fold in order to avoid getting sections oblique to the surface of the disk. Something of an idea of the general appearance of the vesicle can be gained from Bonnet's ('84, Taf. IX. Fig. 2) figure of a sheep embryo of the thirteenth day, which has the same general characters as the pig embryos which I have studied.

The germinal disk of this stage can be detected by the naked eye, even before staining, as a very small opaque white spot on the surface of the vesicle. The smallest vesicle which I have examined is about 1 mm. in diameter, while the largest is about 4.5 mm. In the latter there is no trace whatever of the beginning of the excessive elongation which takes place before the fourteenth day, and has been well figured by Keibel ('93); this growth undoubtedly takes place very rapidly, for Bonnet ('91) has estimated that in the sheep, where a similar though less extensive growth occurs, the embryo must elongate at the rate of more than 1 cm. per hour, and that in the pig the growth is still more rapid. The germinal disk varies in size from 0.1 mm. in the smallest to 0.265 mm. in the largest embryo here considered.

In describing the embryos more at length I shall speak of the layer of nearly isodiametric cells as the ectoderm, and of the inner layer of flattened cells as the entoderm; the relation of these to the outer disintegrating layer, which with Rauber ('75) is best designated as the "Deckschicht," I shall discuss later. The *two prominent* layers (ectoderm and entoderm) are distinguished from each other not only by the shape of their component cells, but also by the shape of their nuclei, and by the chromatic reaction of their protoplasm. The nuclei of the extra-germinal region of the ectoderm are nearly always perfectly spherical; those of the germinal disk, especially in later stages of development, are more often slightly elongated or ellipsoid, with the longest axis at right angles to the surface of the disk; there are significant exceptions to this last rule which will be considered later. The entodermal nuclei in the extra-germinal region are generally flattened parallel to the surface of the embryonic vesicle; those in the region of the disk also have this shape in the younger embryos, but in the older stages they are spherical, and the cells in which they lie are essentially isodiametric. Furthermore, when properly decolorized the hæmatoxylin gives three distinct shades of blue to the embryonic cytoplasm. The extra-germinal ectoderm is stained a light blue, the ectoderm of the germinal disk is sharply marked off from this by a deeper shade, and the cytoplasm of the entodermal cells stains uniformly a still deeper blue. This differentiation in color, which is often of very great value, does not appear before the embryo is decolorized, and it disappears if the process of decolorizing is carried too far, for in that case the whole vesicle becomes a uniform light blue. In almost every instance, these three shades of blue are manifest in my preparations. The chromatic substance of the nucleus stains deeply throughout the vesicle, both in resting nuclei and in those undergoing karyokinetic changes. In the latter, when cut at the proper angle, the nuclear spindle and the protoplasmic radiations around the centrosomes can be clearly seen. It should further be noted, that this stain brings out the cell walls with great distinctness, especially in the ectoderm. In the entoderm the cells are extremely attenuated at their regions of contact, appearing spindle-shaped in section, the nucleus occupying the swollen portion, so that the dividing walls are apparent in the region of the germinal disk only, where the axes of the cell are nearly equal. In my oldest embryos there is no sign of the formation of mesoderm, or of the medullary groove. With this description of the embryonic vesicle in general, I now proceed to the consideration of the more detailed structure of several embryos which I have selected for illustration here. I have chosen these because they show in a typical manner the phenomena which all present, and with drawings from them I can explain intelligibly any variations from the type.

2. *Detailed Account of Observations on the Germinal Disk.*

First Stage. (Plate II Figs. 7, 8, and 9.)

The first embryo which I shall describe is represented by drawings (Plate II. Figs. 7, 8, and 9) of three sections of the germinal disk. This embryo was taken from a sow killed ten days after coitus, which contained eleven embryos. The embryo in question was with one exception the smallest found, but it should be noted here that the ratio between the size of the embryo and that of the germinal disk is not constant for different embryos; and furthermore, that the ratio of the size of the disk to its degree of development varies; e. g. Figs. 11, 12, and 13, Plate II., were drawn from an embryo much larger than that from which Figs. 7, 8, and 9 were made; the two embryos came from the same uterus, and yet the former disk is slightly smaller than the latter; on the other hand, it represents a much later stage of development, as I shall show hereafter, and this fact is doubtless sufficient to account for the difference in size. The whole vesicle from which Figs. 7, 8, and 9 were drawn measured about 1.25 mm. in diameter. As I have already said, the vesicles are flattened out and greatly wrinkled, so that such measurements are at best approximate only, though they serve to give a general idea of the relative sizes of the embryos. The germinal disk, which lies on a part of the vesicle that is not folded, is slightly elliptical in outline, the chief and transverse axes being about 0.11 mm. and 0.167 mm. long respectively; the sections were made nearly at right angles to the shorter axis, which, as I think I can show later, represents the chief axis of the future embryo.

The ectoderm consists of the characteristic large cells with spherical nuclei already described. The entodermal cells form a complete layer on the inner surface of the ectodermal layer, and are more numerous in the region of the germinal disk than in the extra-germinal area, but they everywhere retain their elongated flattened outline. The germinal disk was cut into ten sections, of which Figs. 7 and 8 represent respectively the second and third, and Fig. 9, the sixth. According to my method of orientation the two former are at the posterior end of the future embryo, the latter nearer the anterior end. It will be seen from the figures that the ectodermal cells of the germinal disk are slightly elongated in a direction at right angles to the surface of the disk, and show a tendency to arrange themselves in two interlocking layers. At the margin of the disk the transition from disk ectoderm to extra-germinal ectoderm is abrupt, but the general characteristics of the cells in the two regions is such as to suggest an identity of origin at least, — the differences being merely the slight variation in the chromatic affinity of the cytoplasm, which I have already mentioned, and the change in shape, which would necessarily attend a difference in cell arrangement. The exposed surface of the disk is pretty uniformly even, except at one very significant point. Two sections through this point are shown in Figs. 7 and 8, Plate II., where in the centre of each section a cell is seen to project above the general level of the disk, and in Fig. 8 to be slightly cut off from it. The same appearance is present in the two sections which intervene between Fig. 8 and Fig. 9, and the whole projection running through the four sections contains three cells, which are without any question true ectodermal cells of the germinal disk, which have assumed this new position. These cells represent a very early stage in the development of a structure which I shall later designate as the *bridge*, and for that reason I shall call these *bridge cells*. It should be noted here that there is no evidence whatever of a third layer of cells, i. e. a "Deckschicht," outside the ectoderm in the region of the germinal disk, though in the extra-germinal region there are a few widely separated cells attached to the outer surface of the ectoderm; these differ from the ectodermal cells in having very small nuclei; they resemble the cells of the entoderm in general outline. By an enumeration of the nuclei I have ascertained approximately the number of cells in the area of the germinal disk, which is as follows: cells in the ectoderm proper, 188; in the entoderm, 48; in the bridge, 3. The presence and position of this bridge supply the criterion on which I have determined the chief axis and its poles for the future embryo. It should be further noted here, that in the two sections immediately succeeding Fig. 9, i. e. sections seven and eight of the series through the disk, there is a slight elevation of the ectodermal cells at the margin of the disk on either side. The significance of this fact will appear in my further description of the bridge. Moreover, in sections seven, eight, and nine of the disk there is a distinct groove or furrow in the upper surface of the ectoderm; this runs along the median line, and is therefore in a line continuous with that of the bridge cells described above. And now a word as to similar stages in embryos which I have not figured here.

The ten other embryos which came from the same uterus as the one I have just described vary in size from 1 mm. to 1.9 mm. in diameter, and represent very diverse stages of development. Only two of these are in about the same stage as the one mentioned above, the others being clearly much more advanced, and of these two I consider one further developed than the other, since it has many more bridge cells on the disk. The younger embryo measured 1.4 mm. in diameter, while its germinal disk was 0.11 mm. in diameter and very nearly circular in outline. An enumeration of the nuclei shows approximately 117 cells in the ectoderm proper, 33 in the entoderm, and 6 in the bridge. It is somewhat difficult to determine with absolute certainty the number of cells in the bridge in this case, for some cells are just in process of passing over from the true ectoderm of the disk to the bridge; the direction of the spindle in the karyokinetic figures makes this point indisputable. The mass of bridge cells appears, as in the specimen already described, nearer one margin of the germinal disk, and for that reason I term the margin near the bridge cells the posterior end of the embryo. Anterior to this point there is the same lateral or marginal uprising which I mentioned in the first case. The entoderm consists of greatly flattened cells with widely separated nuclei, but so far as I can determine they are all connected by delicate protoplasmic masses, which often appear like a thin membrane lying across the rounded inner boundaries of the ectodermal cells. One may therefore pass through several sections without finding an entodermal nucleus on a certain area of the embryonic vesicle, but I should not feel justified in assuming that the entoderm fails to cover any portion of the interior surface of the ectoderm of this vesicle.

The second embryo to which I referred in connection with this was but 1 mm. in diameter, and therefore the smallest in my collection. The germinal disk is, however, clearly in a more advanced stage of development, for the reason which I have already given, and the vesicle also has a larger number of entodermal cells, so that there can be no doubt in this case that they form a complete layer on the inside of the ectoderm. On the outside of the vesicle are a very few "Deckschicht" cells. Beyond these facts the embryo presents no characteristic differences from the embryos already described.

SECOND STAGE. (Plate I. Fig. 1; Plate II. Fig. 10.)

I will now take up a stage which shows a distinct advance in the development of the embryo. Fig. 1, Plate I., shows the portion of the blastodermic vesicle containing the germinal disk. This embryo came from the uterus of the sow which was served before coming under my control, so that I do not know the time which elapsed between coitus and the killing of the animal. The stage of development, however, clearly places it at this point in my series. The whole vesicle, which was somewhat wrinkled, was about 2.65 mm. in diameter, while the germinal disk measured 0.205 mm. in its longest axis and 0.18 mm. in its transverse axis. thus having an elliptical or slightly ovate outline, which is shown in the figure. The drawing (Fig. 1) was made from the whole object before staining, and is represented as seen by reflected light against a black background. In sections the entoderm shows the characteristic spindle-shaped cells in the extra-germinal region, while in the area covered by the germinal disk it consists of cells lying closely together and showing sharply defined cell boundaries. On the outside of the blastodermic vesicle are a large number of "Deckschicht" nuclei in the extra-germinal region, all with little chromatic substance and with ill defined cell boundaries. But it is the ectoderm of the germinal disk which presents the most interesting phenomena in this embryo. Fig. 10, Plate II., shows a median longitudinal section through the disk shown in Fig. 1, Plate I. Here the general surface of the disk is seen to be somewhat depressed, thus leaving a raised margin, while at one pole of the longest axis there is a large upgrowth or overgrowth of ectodermal cells forming the bridge to which I have already referred. The beginning of the formation of this overgrowth is at what I hope to establish as the posterior end of the germinal disk. The bridge consists at this stage of practically two layers of cells, which are essentially the same in structure as the remaining ectodermal cells of the germinal disk. Clearly this overgrowth is only a later stage in the growth of the structure which was seen in its first stage of development in Figs. 7 and 8, Plate II., and the raised lateral margins seen here I hold to be comparable with the raised margins described in the previous embryos, while the depressed area seems to be due to a broadening of the median groove of the vesicle, described in detail above. It may be noted here that the germinal disk is unusually large for a bridge which has developed to so small an extent, and furthermore the bridge is more widely separated from the underlying ectoderm than it is in many embryos of this stage.

THIRD STAGE. (Plate I. Fig. 2, Plate IV. Figs. 21 and 26.)

In Fig. 2, Plate I., is shown a surface view of a germinal disk from an embryo taken from still another sow, which was killed ten days after copulation. The blastodermic vesicle was almost completely distended, there being but one marked fold, and measured 1.95 mm. in diameter. The germinal disk was about 0.15 mm. in diameter and circular in outline. It was cut into fourteen sections; these were all drawn with the aid of the camera lucida to an enlargement of 275 diameters, and from these drawings a reconstruction of the surface was made and then reduced to an enlargement of 100 diameters, as it appears in Fig. 2. A reconstruction in wax was also made as a surer means of control to guard against any error in the graphic reconstruction. Two sections of this embryo are shown on Plate IV., Figs. 21 and 26, made through the region of the germinal disk and the extra-germinal area respectively. The sections are oblique to the antero-posterior axis of the disk, cutting it at an angle of about 45°, and running on the reconstruction drawing from the lower right-hand corner to the upper left, Fig. 2, Plate I. Of the fourteen sections into which the disk was cut, Fig. 21, Plate IV., represents the seventh, and passes through the deeper portion of the depression which lies just beneath the central point of the free margin of the bridge, as seen in Fig. 2. In this specimen the two lateral elevations mentioned in the embryos already described are seen to have increased in size until they have come into contact with the posterior overgrowth, with which they have fused at two points, thus giving the bridge three points of attachment to the ectoderm proper and leaving three openings from the depression or cavity beneath it to the outside. This bridge, then, has manifestly three points of origin, one posterior and two lateral. Further evidence in corroboration of a similar method of formation will appear in the course of the description of the other embryos.

Before leaving the ectoderm of the germinal disk, it should be added that it is relatively very thick in all these younger embryos, consisting of two or even three interlocking layers of cells, in addition to the bridge cells, which are usually two layers deep. This great thickening of the ectoderm of the germinal disk is not, however, the earliest condition ontogenetically, for in younger stages of development, as, for example, those represented by Figs. 7–10, Plate II., it is much thinner than in either the stage under discussion or that represented by the figures on Plate III.

The cells of the entoderm are essentially the same in structure in the region of the germinal disk as they were over the same area in the embryo represented in Fig. 1, Plate I., and Fig. 10, Plate II.; but there is a further thickening or increase in number of the entodermal cells immediately surrounding the germinal disk, and extending on all sides of it for a distance about equal to the diameter of the disk itself, so that the diameter of the entodermal thickening is at this stage about three times the diameter of the germinal disk. The normal distribution of the entodermal nuclei in the remainder of the extra-germinal area can be seen from Fig. 26, Plate IV. A possible explanation as to the significance of this thickening of the entoderm has occurred to me, which I will mention in the theoretical considerations concerning the interpretation of the vesicle.

FOURTH STAGE. (Plate I. Figs. 3–5; Plate II. Figs. 11–13; Plate III. Figs. 14–19; Plate IV. Fig. 20.)

The next two embryos in the series are shown in Figs. 3 and 4, Plate I. I have given no sections of these, as the surface views show the more important characteristics, and because they are essentially the same as sections of other embryos which I have figured farther on. Fig. 3 shows that the bridge has a nearly circular margin bordering the opening into the cavity beneath. There is no evidence on the surface of the germinal disk or in the sections — which are taken at right angles to the longer (i. e. transverse) axis — as to whether the bridge arose at three points, as mentioned above, and then became one by a fusion of the three parts, or whether it arose as one continuous overgrowth from the margins towards the centre of the disk. The vesicle to which this germinal disk belongs was 2.25 mm. in diameter and very little folded. The disk itself measured 0.19 mm. in its longer axis and 0.15 in its shorter or antero-posterior axis. It will be observed that the elliptical outline of the germinal disk is the same with regard to the chief axis of the future embryo, as in the case of the first embryo described.

Figure 4 represents a disk which is a little older than that shown in Fig. 3. The bridge covers a larger portion of the germinal disk than in the preceding case, and if we assume that the disk had at first the shape shown in Fig. 3, it has begun to elongate in the direction of its chief axis, until it is now nearly circular in outline. The right-hand side of the figure shows a lateral opening into the cavity beneath the bridge, where the lateral overgrowth has not as yet entirely fused with the overgrowth from the posterior end to form a continuous bridge such as exists in Fig. 3. The left-hand side, however, is complete, exactly as in Fig. 3. This germinal disk might be considered as illustrating a stage intermediate between Figs. 2 and 3, so far as the fusion of the various parts of the bridge is concerned; it is, however, clearly more advanced, not alone on account of the greater size of the germinal disk, — for this may vary greatly, as we have already seen, — but because of the greater extent and degree of development of the bridge. The embryonic vesicle in this case was only slightly folded, nearly circular in outline, and about 2.75 mm. in diameter; the germinal disk measured 0.2 mm. in diameter.

Figures 11, 12, and 13, Plate II., represent sections through a germinal disk in which the bridge has reached about the same stage of development as in the two cases last described. The embryo from which these three sections were taken came from the same uterus as that of Figs. 7, 8, and 9, and the sow was killed therefore on the tenth day after coitus. This vesicle measured about 1.55 mm. in diameter, while the disk, which was slightly elliptical, measured 0.145 mm. in its longer axis (the sections shown in Figs. 11, 12, and 13 are parallel to this axis), and 0.11 mm. in its shorter axis. This shows, then, a still greater elongation than the preceding germinal disk in the direction of the chief axis of the future embryo. The disk was cut into eleven sections, of which Fig. 11 represents the fifth; it is, therefore, a little to one side of the median plane. This section shows well a phenomenon which is present in all sections of bridges that have developed to some extent, and seems to point to a double origin of this structure. It will be noticed that the extra-germinal ectoderm appears to extend as a continuous layer over the right-hand portion of the disk and to constitute the upper layer of bridge cells, while the lower layer is clearly derived from the true ectoderm of the germinal disk itself, as we can see from the position of the nuclei at the region of contact of the bridge with the underlying ectoderm. It should be observed, however, that this apparent extension of the extra-germinal ectoderm over the ectoderm of the germinal disk occurs in the region of the bridge only. The whole appearance suggests an upfolding of the margin of the disk, which carries both the extra-germinal and the germinal ectoderm with it. Figs. 12 and 13 represent the eighth and ninth sections respectively through the same disk. Fig. 12 is a section at the extreme lateral margin of the opening of the bridge, the cavity beneath it appearing as a somewhat triangular space in the section.

Fig. 13 lies beyond the region of the cavity, and the bridge is here in contact with the underlying ectoderm.

I am so fortunate as to have another embryo from the same uterus from which this came, which is in almost precisely the same stage of development, and is cut very nearly at right angles to the chief axis of the germinal disk. This gives a series of sections transverse to those which I have just described. The general relation of the overgrowth, or bridge, to the underlying ectoderm will be plain, if I describe briefly two or three of the sections. Beginning with the second section in the series, which lies at what I term the posterior end of the embryo, a condition is found which is very like that represented in Fig. 13, Plate II., consisting of a layer of true, somewhat columnar ectodermal cells, with the long axis perpendicular to the surface of the disk, and overlaid by a layer of bridge cells, slightly elongated in a direction parallel to the surface of the disk. The next section anterior to this shows the bridge passing across the germinal disk from one side to the other, and separated from it in the central region by a cavity; the structure here resembles an arch spanning the disk from side to side. Taking next a still more anterior section, the bridge is represented by an upfolded region at either side of the germinal disk, overhanging the true ectoderm, and presenting very much the appearance that Fig. 10, Plate II., would present if there were also an upfolding at the right-hand side of the drawing similar to that at the left. The succeeding sections simply show these lateral upfoldings diminishing in size until they disappear near the anterior margin of the germinal disk. Thus this series of sections, together with the series described just before it, gives the basis for a very complete conception of the bridge as it appears at this stage.

Returning now to the figures, we find a condition somewhat more advanced than the preceding, represented by Fig. 5, Plate I. The vesicle from which this germinal disk came was taken from the uterus on the eleventh day after coitus, together with three others, which were all manifestly older. The vesicle was somewhat wrinkled, and measured 3.4 mm. in its longest diameter. The disk lay near one margin in an unwrinkled area, and was ovate in outline, the long axis being 0.23 mm. and the greatest transverse axis 0.2 mm. in length. At the broad or anterior end the crescent-shaped free margin of the bridge appears sharply marked off from the underlying ectoderm by a cavity which extends to within a short distance of the margin of the disk on all sides except at the anterior end, where the bridge is wanting. At this point the ectoderm is slightly thicker than in the region beneath the bridge, and this thickening appears on the surface as a slight elevation, which I have tried to show by the shading in the drawing. This germinal disk illustrates the form and structure of the bridge so clearly and so typically, and represents almost, if not quite, its maximum development as a free and independent structure, that I have thought best to illustrate it more fully by sections than I have done in the case of the preceding embryos.

The sections were made in a direction very nearly parallel to the long axis of the germinal disk, which at this stage corresponds to the antero-posterior axis of the embryo. The disk was divided into fifteen sections, and of these, Figs. 14–19, Plate III., and Fig. 20, Plate IV., represent respectively the first, second, fourth, sixth, seventh, eighth, and ninth; the sections beyond these simply present the same phenomena in reversed order. Little need be said in explanation of the first two sections, Figs. 14 and 15, Plate III. Figure 14 is taken at the extreme lateral margin of the disk and is consequently nearer the anterior than the posterior end, because of the ovate outline of the disk. The section immediately preceding this consisted merely of a layer of typical ectodermal cells on the outside with a layer of characteristic entodermal cells a short distance beneath. Figs. 14 and 15 show the great rapidity with which the ectoderm increases in thickness in passing from the lateral margin of the disk towards its centre. The third section in the series has not been represented here, since it shows no new features beyond those represented in Fig. 15, except an extension of the ectodermal cells in a posterior direction. The next section is represented by Fig. 16, in which occurs the first appearance of the cavity which marks off the bridge from the rest of the germinal disk. The bridge itself consists of several irregular layers of cells, the outermost of which is made up of cells considerably flattened in the plane of the germinal disk. As to the general characteristics of the disk in section, it should be noted that the anterior (in the figure, the right-hand) end is thicker and more rounded than the posterior, which is rather attenuated. It will also be seen that the lower or inner boundary of the ectodermal cells of the disk is marked by a relatively sharp line due to the presence of a very delicate membrane. At the margin of the germinal ectoderm, — where, between the extra-embryonic ectoderm and entoderm, a space (triangular in section) occurs which completely surrounds the disk, — this membrane loses its connection with the ectoderm of the germinal disk and stretches across the space to meet the extra-embryonic portion of the outer layer at some distance from the margin of the disk. The whole entoderm is normally in close contact with the ectoderm, but in the region of this membrane it seems to be more loosely attached than elsewhere, or else the cells are less resistant, for we often find that here they are somewhat torn away, as though by some mechanical injury, possibly due to the effect of the fixing or the hardening reagents, which necessarily produce a slight shrinking of the vesicle. This membrane will be more fully discussed farther on.

I have not introduced the figure of the next section in the series, since it merely shows a condition intermediate between the preceding and following sections. Fig. 17 passes near the lateral margin of the free edge of the bridge, and shows that the cavity beneath the bridge extends much farther towards the posterior end of the germinal disk, and also that the bridge itself is thinner just at this point than in the preceding and the succeeding sections. By comparing this with both Figs. 18 and 19, it will be readily seen that this diminution in thickness results in a ring or crescent very near the inner margin of the under side of the bridge, which in Fig. 17 is cut nearly longitudinally, and in Figs. 18 and 19 transversely near the posterior point of attachment of the bridge to the underlying ectoderm. Fig. 18 shows the first section which passes through the free anterior margin of the bridge.

Figures 19 and 20 may best be considered together. Fig. 19 represents the section which lies in the median plane of the embryo, and consequently here the free edge of the bridge is farthest removed from the anterior end of the disk. In Fig. 20, Plate IV. the free margin of the bridge has begun to advance towards the anterior end of the disk again. The phenomenon of greatest significance in these sections, however, is found at the point where the bridge comes in contact with the ectoderm of the germinal disk near the posterior pole of the chief axis. In Fig. 19 it will be noticed that the cavity beneath the bridge appears to extend between the cells posteriorly as a narrow opening for a short distance. In Fig. 20 we find a continuous canal passing from the cavity beneath the bridge into the space between the ectoderm and the entoderm of the extra-germinal area just at the margin of the germinal disk. This canal appears to arise in the median plane of the embryo, and to pass between the ectodermal cells into the cavity just mentioned in a direction slightly oblique to that plane. At least that must be the conclusion, provided the sections are exactly parallel to the median plane of the disk; but if the sections were only very slightly oblique, they would make a canal as small as this appear to have an oblique direction, even though it were actually parallel to the chief axis of the embryo. This phenomenon is not confined to this embryo. A precisely similar canal can be traced in the embryo figured on Plate I. Fig. 3, and in two or three other cases there are suggestions of a similar condition, but not sufficiently well marked for me to put much stress upon them. It will be readily seen that unless the section should pass in exactly the right direction, i. e. very nearly through the long axis of the canal, it would be impossible to establish its presence except in extremely thin sections. Its occurrence in Fig. 20 is beyond question; I shall discuss its possible morphological significance later.

The fact that the free surface of the germinal ectoderm shows no trace of cells resembling the ectoderm of the extra-germinal area, such as are present on the upper surface of the bridge, may be mentioned here again in passing.

FIFTH STAGE. (Plate I. Fig. 6; Plate IV. Figs. 22–25.)

We now come to the last stage in the history of the bridge. This can best be shown in two phases, the first of which is represented by Figs. 22 and 23, Plate IV. These are from sections of an embryo taken from the same uterus as that represented by Fig. 2, Plate I. The blastodermic vesicle was small in comparison with the size of the germinal disk, being but 3.1 mm. in diameter, while the disk, which was ovate in outline, measured about 0.3 mm. in its long diameter, and in its greatest width 0.29 mm. It was cut into thirty sections in a direction nearly perpendicular to the long (chief) axis. Fig. 22 represents the thirteenth section in the series, which begins at the narrower or posterior end, and Fig. 23 represents the seventeenth, which is therefore somewhat more anterior. Fig. 22 shows that the germinal disk consists of cells whose nuclei lie at varying distances from the surface of the disk, and that it has a rather broad median region pretty clearly marked off from a marginal region on either side, by the fact that it contains more nuclei, and also because the general surface of the median region is here slightly elevated above the lateral portions of the disk. This median elevation is more or less marked in the sections which precede this in the series, maintaining about the same relative extent. In the succeeding sections, however, it is no longer marked, so that the surface of the ectoderm is pretty uniformly flat. At the same time there is to be noticed at the margin a layer of cells cut off from the underlying ectoderm by a narrow cavity. This occurs on each side of the disk, but owing to the obliquity of the sections it appears in Fig. 23 at the left-hand side only, while it is seen at the right as well in the sections immediately following. The stage of development represented by these sections can, I think, be readily shown to be only a more advanced condition of the phenomena presented by the germinal disk of Fig. 5. The change is brought about by a simple obliteration of the cavity between the disk and the bridge, produced by the sinking down of the bridge until it comes in contact with the surface of the disk, with which it fuses. The cavity which appears at the left in Fig. 23, and on the right in succeeding sections, is in all probability the last trace of the marginal groove which I mentioned in the description of the preceding embryo as running around the under surface of the bridge.

Another embryo shows a second and later phase in the disappearance of the bridge. Fig. 6, Plate I., represents the germinal disk of an embryo taken from the same uterus as that of Fig. 5. The blastodermic vesicle was nearly circular in outline, slightly folded, and measured 3.9 mm. in diameter. The germinal disk was distinctly ovate in outline, as shown in Fig. 6, and measured in its long axis 0.265 mm. and in its greatest breadth 0.23 mm., thus exceeding in size the disk of Fig. 5 by just 0.03 mm. in each diameter. Though somewhat smaller than the disk just described, it is clearly older, as the description of the sections will show. It was cut into thirty sections in a transverse direction, i. e. at right angles to the long axis of the embryo. Starting from the broader end of the disk, Fig. 24 represents the fourth section in the series, and Fig. 25 the seventh. Here the only evidence we have that a bridge has been present is in the shape and position of some of the more superficial cells and their nuclei. In Fig. 24 several of the surface cells show the characteristic elongated outline with flattened nuclei which the more superficial cells of the bridge present in its greatest development, and in Fig. 25 two cells near the centre show, for the same reason, an undoubted origin from the bridge.

3. *Summary of Observations on the Blastodermic Vesicle of the Pig.*

I have given above in some detail the principal phenomena which my material presents, and now I wish to give in a more compact form what I take to be the typical changes which occur in the period of development which these embryos cover, and to point out one or two variations from the type which serve to throw some light upon its meaning.

The earliest stage which I have, shows a blastodermic vesicle consisting of a sharply defined inner layer of flattened cells, — the entoderm, — which forms a closed sac. In contact with the outside of this is a layer of nearly isodiametric cells, — the ectoderm, — which at one point is thickened to form the germinal disk, both by an increase in the diameter of the cells at right angles to the surface, and by an increase in the number of cell layers. On the outside of the ectoderm is found here and there a "Deckschicht" cell, apparently in process of disintegration. In short, the blastodermic vesicle has seemingly completed only recently the so-called first phase in mammalian gastrulation, as advocated by Hubrecht ('88 and '90) and Keibel ('89 and '93). The germinal disk is slightly elliptical in outline; not far from one pole of the shorter axis a proliferation of ectodermal cells has taken place, so that three cells have come to lie above the general surface of the disk. Consequently, and for additional reasons which I shall give later, I consider the shorter axis to be the chief axis of the embryo, and the pole where the proliferation of cells takes place the posterior pole. There is, furthermore, anterior to this proliferation, a slight elevation at the two lateral margins of the disk, while along the median line between them there is a depression.

As the embryo develops, the germinal disk grows by a multiplication of cells; the area covered by the disk is, however, augmented slowly, the tendency being, for a certain period, to an increase in thickness. Thus the germinal disk, sections of which are shown in Figs. 14 to 21 on Plates III. and IV., is relatively much thicker than those represented by Figs. 7 to 10 on Plate II. While the disk increases thus in thickness, the proliferation of cells at the posterior end continues, producing a distinct upfolding or overgrowth in that region, and at the same time a similar process has been going on at the two lateral margins. Soon these three overgrowths meet and fuse, forming one continuous bridge, at first attached at only three points, but later coming in contact with the disk at all points of the margin, save the anterior. There is present also a depression on the surface of the ectoderm of the disk immediately beneath the bridge, and the cavity which lies between this surface and the under surface of the bridge is connected by a narrow canal with the cavity which surrounds the disk between the extra-germinal ectoderm and the entoderm. The bridge, furthermore, seems to grow not only by a proliferation of the ectodermal cells of the germinal disk, but also by additions from the adjacent cells of the extra-germinal area.

There is strong evidence of such a method of development as I have just traced, not only in the figures which I have reproduced here, but also in the case of several embryos in which the disk is much larger than at this stage, and has clearly made a greater ontogenetic advance. In these a large well developed bridge is found, overlying a depression in the germinal disk below, to which it is attached at only three points, one of these being usually larger than the others, and apparently representing the posterior overgrowth, which seems to develop slightly in advance of the lateral proliferations. An anomalous condition of the bridge is interesting. In one embryo measuring 4 mm., with a germinal disk 0.28 mm. in diameter, the lateral proliferations seem to have been entirely suppressed, and we have an overgrowth from only one region, the posterior, extending forward along the median line of the disk.

The fate of the bridge seems to be, that its free anterior margin finally meets the true ectoderm of the disk ; the structure then sinks down until it comes in contact with the underlying ectoderm, with which it finally fuses. At the same time the disk increases in area, this being largely due to a rearrangement of the cells of the disk in consequence of the addition received from the bridge. This method of increasing in size at this stage was first suggested to me by the fact that few nuclei are found in a karyokinetic condition. Accordingly, in the case of the two germinal disks represented by Figs. 5 and 6, Plate I., which correspond to the two stages of development in question, I counted the number of nuclei in each, as seen in sections, to determine the numerical relations of the cells. In the disk of Fig. 5 I found 1067 cells, in that of Fig. 6, 992; although embryos in their early development grow at very different rates, still the facts which these numbers present, together with the absence of nuclear figures, would seem to point to a simple rearrangement of existing cells as the principal factor in the increase in area of the germinal disk at this stage, rather than to an active multiplication of cells.

The oldest embryos considered in this paper consist, then, of a blastodermic vesicle, composed of a continuous inner sac of entoderm closely surrounded by a layer of ectodermal cells, which in the germinal disk are thickened into a flat, ovate expanse, without primitive groove or streak, with no signs of any mesoderm, and with a few widely scattered "Deckschicht" nuclei on the extra-germinal area. The entodermal cells are thickened in the region of the germinal disk until they become nearly isodiametric, and they are also thickened, though to a less extent, in an area all around the germinal disk, the diameter of which is about three times as great as that of the disk itself. With this summary I now pass to a consideration of the observations of other investigators on the mammalian blastodermic vesicle, and to the theoretical interpretation of some of the phenomena which occur in the embryo of the pig, as I have described them.

III. Historical and Theoretical.

1. *Consideration of Observations on the Blastodermic Vesicle in General.*

On account of the incompleteness of our knowledge of the facts concerning the blastodermic vesicle of the Mammalia, there are naturally several theories with regard to the exact method of its formation, and the interpretation of the vesicle when once it has been formed. Since my own material begins with the completely formed blastodermic vesicle, I cannot from an actual observation of the process of development add anything to our knowledge of the method of it formation; but the phenomena which the vesicle at this stage presents, taken in connection with the observations of other investigators on mammalian embryology, serve to throw not a little light on several of the mooted points of its development.

Although the accounts of mammalian cleavage are few, and not in accord with one another, it seems to be pretty well established that cleavage results in the formation of a hollow sphere of cells, containing on the inside, at one pole, a more or less irregular mass of cells. These facts have been recorded by various authors; as, for example, Lieberkühn ('79), Van Beneden ('80), Van Beneden et Julin ('80), Heape ('83), Hubrecht ('90), Duval ('91), Robinson ('92), Christiani ('92), and others. The method of formation of the germinal layers from these structures is in much dispute, however. I will consider briefly four theories which have been advanced on this subject, upon which my own investigations seem to throw some light; but I would not be understood as trying to make all the observed methods of mammalian development conform to one type, — there certainly are not as yet sufficient data for that; and besides, many reasons exist for supposing that there may be several types of development, conforming to the varied conditions under which the very young embryo is placed in different mammals.

The first theory is that which Van Beneden ('80) formulated for the rabbit. He found a well defined outer layer of cells, just beneath this in the region of the germinal disk a layer of flattened cells lining a limited area, and within this a layer which had extended partially around the inner wall of the outer layer, and these three layers he believed to represent the ectoderm, mesoderm, and entoderm respectively.

Other investigators have found different conditions, however, which disprove this theory. I merely mention it; first, because my own embryos show clearly a marked outer layer, which I have termed ectoderm, lined with a flattened layer, the entoderm, and outside of all, unmistakable "Deckzellen," which would have to be derived from the outermost layer of cells at a stage such as Van Beneden described; and, secondly, because not long ago Duval ('91) found, as described in his work on the rat and the mouse, young embryos to which he gave an interpretation very similar to that of Van Beneden for the rabbit. He describes a hollow vesicle, consisting of an outer layer of nearly isodiametric cells (see Duval, '91, Plate I., Figs. 73 and 74), with a number of larger, somewhat irregular cells inside, attached to the outer layer at one pole. He considers these two sets of cells ectoderm and entoderm respectively. As Duval describes the subsequent development, it is difficult to interpret these otherwise; but it should be remembered that Selenka ('83) considered the outer layer a "Deckschicht," and that Robinson ('92), working on the same animals, has reached conclusions widely different from those of Duval. I should like further to call attention to Duval's Figs. 75 and 79, Plate I., which resemble strongly those of other investigators on the rabbit, the mole, and the shrew, and which would seem to represent a vesicle consisting of an outer layer of somewhat flattened cells, and an inner mass *differentiated* into two distinct regions, very much as Heape ('83, Plate XXIX. Fig. 20) has shown it in the mole.

The second theory is held by a larger number of investigators, perhaps, than any other. It maintains that the flattened cells of the outer layer become columnar and form the ectoderm of the extra-germinal region. The inner mass of cells differentiates into two superposed parts; the inner becomes the entoderm and comes to line the inner surface of the ectoderm; the cells of the outer part become columnar, and, fusing with the cells of the outer layer, form the ectoderm of the germinal disk. Balfour ('81), in conjunction with Heape, thought he was able to trace the actual process of transformation of the flattened into columnar cells. Essentially the same views are advocated by Rauber ('75), Lieberkühn ('79), Kölliker ('80), and Hubrecht ('90).

My material supplies no evidence whatever of any transformation of the outer layer of cells, or "Deckschicht," into true ectodermal cells; on the other hand, these "Deckzellen" show unmistakable signs of disintegration. The embryos represented in part in Figs. 1, 3, and 4, Plate I., have these cells in a better state of preservation than most of the others figured here. Fig. 27, Plate IV., is from a section through the extra-germinal area of the embryo of Fig. 3. Here, at the left and the centre, we see two "Deckschicht" cells, which are entirely characteristic, the boundaries rather indistinct, the nuclei round and with very little chromatic substance, the whole cell flattened in the plane of the surface of the ectoderm; these occur all over the vesicle at about the same distance apart. At the right-hand side of the figure I have shown several such cells in contact with one another; this is the only place in my material where I have found this phenomenon; it suggested a possible earlier condition of these cells. The cell boundaries, however, are very indistinct; the cytoplasm is scarcely stainable at all, while the contents of the nucleus stain a nearly uniform light blue. I am inclined, then, to regard these cells as belonging to a purely transitory layer, which may for a time serve some protective or other function, and then disappears by the disintegration of its elements as it gradually becomes of no further use. Bonnet ('91) says that this layer disappears early in the sheep and in the pig, and he finds no trace of it in the youngest sheep embryo he has described (Bonnet, '84, Taf. IX. Figs. 2 and 3.) It should be remarked that in my oldest embryos, e. g. Fig. 6, Plate I., there is scarcely any evidence that a "Deckschicht" has been present, — only here and there a small nucleus attached to the surface of the ectoderm.

The third theory mentioned is that advocated by Minot ('85 and '89) and at the same time by Haddon ('85 and 87) and later by Keibel ('87). This theory starts, like the others, with an outer layer, and at one pole an inner attached mass, and assumes that the whole outer layer is entoderm, while the inner mass differentiates into two superposed layers, an outer, which becomes the true ectoderm when the entoderm outside of it, as a Rauber's "Deckschicht," disappears, and an inner, which becomes the entoderm of the germinal disk. Minot ('89) further suggests a complete inversion of the layers for all placental Mammalia. Earlier stages than mine are necessary for a full discussion of this question, but the three-layer condition which I have found over the greater part of the blastodermic vesicles of the pig, seems to me an insurmountable objection to this theory. If the primary vesicle is of entoderm, and the ectoderm later grows around it to produce the didermic blastocyst, to what origin are we to ascribe the outer layer of " Deckzellen " which I have described?

The last theory which I shall mention is that suggested by Robinson ('92). His studies on the embryos of the rat and the mouse have led him to believe that the portion of the outer layer lying beyond the germinal disk is entoderm, while the ectoderm is limited to the outer layer of the germinal disk region. In the rat and the mouse he does not find the ectoderm overgrowing the entoderm. However correct this theory may be for the rat and the mouse, (my own work on these animals leaves me still undecided on this point,) my investigations on the pig show conclusively that the entodermal vesicle becomes entirely surrounded by ectoderm.

I can add little towards determining whether in the pig the extension of the entoderm over the inner surface of the ectoderm takes place by a growth proceeding from the margin of the entodermal portion of the germinal disk, as in the rabbit, mole, etc., or whether this entodermal mass of the germinal disk becomes a hollow vesicle, which reaches the ectodermal wall by a multiplication and expansion of its cells, such as would seem to take place in the hedgehog (Hubrecht '89, Figs. 7, 8, and 9, Plate XV.) and in the cat (Schäfer '76, Fig. 1, Plate X.). The youngest embryo which I have described, from which Figs. 7, 8, and 9, Plate II., were made, showed, as I have already said, an area at the end of the vesicle farthest from the germinal disk, where for several sections no entodermal nuclei appeared. If I had had several embryos presenting this same phenomenon, I should be inclined to think that the entoderm was in process of lining the ectodermal vesicle and had not yet completed its work; but, as I said in my description of this embryo, the entodermal cells are so widely separated over the whole vesicle that I do not feel justified in asserting that there is a space really free from entoderm at this stage. Bonnet ('84), in his description of a sheep embryo of thirteen days, finds the entoderm in very much the same condition; he says: " Die Keimblase ist, wie auch die Schnitte beweisen, durchweg doppelblättrig. Die Entoblastzellen bilden aber in einiger Entfernung vom Schild keine continuirliche Lage, sondern eine netzförmig durchbrochene Membran anastomosirender Zellen von 15–24 μ Länge." Van Beneden ('80) finds that it is absent at one pole of the vesicle, and the same condition has been observed by both Heape ('83, Figs. 20–23, Plate XXIX.) and Keibel ('89, Fig. 46 *a*, Taf. XXIV.). Hubrecht ('90) quotes Hensen ('76, Fig. 18, Taf. VIII.) as authority for the presence of the entoderm at this region, and the figure would certainly seem to suggest this; but we should at least not ignore Hensen's own statement of the case when he says, "Die innere Keimhaut geht nur über das obere Drittheil des Eies; wenn an andere Stellen die Keimhaut zweischichtig erscheint, so möge man dies aus der Drehung beim Uebergang von der Flächen- in die Kantenansicht erklären." The figure, however, does give the appearance of two layers at the region under discussion. While such observations as those of Heape ('83) and of Schäfer ('76) would seem to point to two distinct methods of the extension of the entoderm in Mammalia, I cannot affirm with certainty that either occurs in the pig; what evidence I have, I am inclined to interpret in support of the phenomenon as it is said to occur in the rabbit, the mole, etc.; i. e. as a process of marginal growth from the inner mass of cells of the germinal disk.

The process of entoderm formation from the inner mass of cells would seem to be primarily, then, a separation of certain cells from the general group, and I cannot help drawing attention here to the fact that there may be an homology between this process and the method of entoderm formation described by Robinson and Assheton ('91) in the frog; furthermore, the formation of the didermic stage in the rat, as interpreted by Robinson ('92), is comparable with this, for he finds first a mass of irregular cells, in which a cavity develops separating a single layer of cells at one pole from a mass of cells at the other; the single layer he considers ectoderm, and the cells at the opposite pole the entoderm, or, as he calls them, epiblast and hypoblast respectively. I am not, however, sure in the light of the results of Selenka ('83) and Duval ('91), that this interpretation is correct.

Before leaving the general consideration of the blastodermic vesicle, there are two or three other points to which I wish to refer. Schäfer ('76) found in the embryo of the cat a clearly defined non-cellular membrane over the outer surface of the entoderm in the region of the germinal disk; this he calls the "membrana limitans hypoblastica," and compares it to the "membrana prima" described by Hensen ('76) in the first part of his paper on the rabbit (see Hensen, Fig. 19, Taf. IX.). In the second part of his paper, Hensen figures the membrane as in contact with the entoderm in the region of the primitive streak only, and as then passing over the dorsal side of the mesodermal somites, and coming in contact with the ectoderm laterally (see his Fig. 37, Taf. X.). In Hensen's earlier figure, and in Schäfer's, this membrane is clearly an entodermal structure, and I hold it comparable to the membrane which I have found between the ectoderm and the entoderm of the germinal disk, which leaves the ectoderm at the margin of the disk and passes off to meet the extra-germinal ectoderm farther on. This membrane would be of great assistance, it seems to me, in determining the origin of the mesoderm within the germinal area. Many authors have not figured this structure, as, for example, Kölliker ('82), Heape ('83), Bonnet ('84), Hubrecht ('90), and others. In the rat and the mouse I have noticed a sharp line between ectoderm and entoderm, which is probably the same structure, and it has been figured by other investigators of these animals (see Duval '91, Robinson '92, and others).

There is another point to which I wish to draw attention, without however attaching too great significance to it. In the description of my younger embryos I mentioned the fact that the germinal disk was elliptical in outline, and that, according to my orientation, the shorter axis of the ellipse lay in the plane of bilateral symmetry of the future animal. Though it may be of little morphological significance, it is certainly very interesting to note that in its earlier stages the blastoderm in teleosts (which must be held to be homologous with the germinal disk of the mammalian embryonic vesicle) is also elliptical in outline, and furthermore that the shorter axis of the ellipse corresponds to the chief axis of the future fish, as established by Agassiz and Whitman ('84). This elliptical outline, which seems to be constant in teleosts (see Ryder '84, Agassiz and Whitman '85 and '89, Wilson '91, etc.), is produced in the first place by the first cleavage plane, which divides the protoplasmic mass at the active pole of the egg into two parts, each circular in outline, so that as they lie side by side the blastoderm is elongated; this condition persists for some time.

If the first plane of cleavage in the teleost is not identical with the plane of bilateral symmetry, my comparison, of course, has no validity. So far as I am aware, there has been but one series of experiments whose results would seem to disprove this theory; and these were conducted by Miss Clapp ('91), who worked on the eggs of Batrachus tau. These eggs — attached by means of their thick outer membrane to the vessel in which they were placed — were artificially fertilized, and the position of the first plane of cleavage noted. Some seven days later the chief axis of the future fish was clearly visible, and was superposed on the line of direction of the first cleavage plane. In only three cases out of twenty-three did the two lines coincide; in the rest the second line made a greater or less angle to the right or left of the first, — never greater than 70° however. But I think there is a possible source of error here, which makes my comparison still permissible. The author states that rotation is impossible, since the yolk is attached to the egg membrane at the point where the membrane attaches itself to the vessel, but offers nothing in evidence of this statement. Ryder ('86), however, infers that the yolk does not become attached until "after the vitellus has been covered by the blastoderm." During last summer, when through the courtesy of Dr. Alexander Agassiz I had the privilege of studying several weeks at the Newport Marine Laboratory, I collected material of the cleavage stages of Batrachus tau. This material was fixed without puncturing the egg membrane, and a careful examination of it shows no trace of any attachment of the yolk to the membrane, although the contents of the egg are everywhere in contact with it. It should further be remembered that the contents are in a semi-fluid condition, and during the seven days mentioned abundant opportunity is furnished for a rotation of the yolk within the egg membrane.*

Before leaving this matter of the shape of the germinal disk, I wish to refer to a young disk of the shrew, which Hubrecht ('90) has figured (Plate XXXVII. Fig. 17) as elliptical, very much as I have described the disks of the pig. From the position of the figure on the plate I am left to infer that the shorter axis of the disk becomes the principal axis of the embryo. In the later development he finds the disk ovate, but he places the narrow end anterior and the broad end posterior, except in one case (Plate XXXVII. Fig. 21), where the broad end is anterior, just as I have placed it in my descriptions of the pig. This ovate outline, oriented thus, is certainly characteristic of slightly later stages, and has been figured many times; e. g. by Kölliker ('82) in the rabbit, Duval ('89) in the chick, Keibel ('93) in the pig, etc.

I now come to the last point which I wish to consider before taking up the interpretation of the bridge. In the embryo represented by Fig. 2, Plate I., and in all the following embryos figured on this plate, there occurs a thickening of the entoderm, not only in the region of the germinal disk, but also in a considerable area immediately surrounding it. By a thickening I do not mean that the entodermal cells have multiplied so as to be superimposed upon one another to form a mass more than one layer deep, but simply an increase in the number of cells over a certain area, so that they come to lie more closely together, and in consequence give the appearance in surface view of a thickened entodermal area. The question of course concerns the significance of this circum-germinal thickening. An explanation has suggested itself to me, which rests, however, on a theory which I do not feel at all sure is established. The theory concerns the origin of the mesoderm. Hubrecht ('90) gives three sources for the mesoderm: the protochordal plate, the primitive streak ("gastrula ridge" and "Kopffortsatz"), and "an annular zone of hypoblast situated just outside the limits of the embryonic shield, and thus enclosing — but at the outset independent of — the protochordal plate." The annular zone according to Hubrecht does not arise until after the first stages in the development of the primitive streak, and therefore is a *later* differentiation in the hypoblast than is the protochordal plate.

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* Very recently Morgan, (Experimental Studies on the Teleost Eggs, Preliminary Communication, Anat. Anzeiger, Jahrg. VIII. pp. 803-814, 1893,) working on the eggs of Ctenolabrus and Serranus, has arrived at the conclusion that "there is no relation whatsoever between the cleavage planes of the egg and the median plane of the adult body." Dr. Morgan bases this statement on the observation of the axes of twenty-two eggs, and his method of determining the position of the axes appears to be satisfactory. I cannot, however, enter upon a fuller consideration of the subject here.

Concerning this third source there has been much dispute. Bonnet ('84) has found it in the sheep, and Robinson ('92) in the rat and the mouse. But many authors find no evidence of such an origin for any part of the mesoderm, as, for example, Kölliker ('82), Heape ('83), Fleischmann ('89), Keibel ('91 and '93), Hertwig ('93), and very many others. It has occurred to me that this circum-germinal thickening might be the first evidence of a later (ontogenetically) formation of mesoderm in this region. Since Keibel's ('93) youngest pig embryo has the mesoderm already well advanced in development and covering the area in question in two layers, somatic and splanchnic, it is impossible to say what the stages intermediate between his and mine may have been, and I merely mention the above suggestion as a possible explanation of an interesting phenomenon. There is, as I have already said, no trace in my specimens of mesoderm in any region of the vesicle, and no sign, either in surface view or in section, of a thickening of entodermal cells in any part of the germinal disk, like the protochordal plate which Hubrecht ('90) describes for the shrew. To make sure that this was not merely a subjective impression I enumerated the nuclei in each section of the germinal disk of Fig. 6, Plate I., beginning at the broader end, and the result was as follows: 3, 8, 10, 10, 14, 15, 18, 18, 20, 23, 28, 24, 23, 25, 24, 31, 30, 23, 22, 17, 15, 12, 10, 9, 10, 11, 6. A comparison of these figures with the shape of the disk will show an almost uniform distribution of entodermal cells.

2. *Interpretation of the Bridge.*

I now have to consider the interpretation of the structure which I have called the bridge. There are two structures which have been described in vertebrate ontogeny with which it may perhaps be possible to compare it. One of these has been figured by Heape ('83, Plate XXIX. Figs. 20–28) in the blastodermic vesicle of the mole. He here shows a thickened ectoderm in the region of the germinal disk, with a layer of entoderm beneath but not extending far beyond it, and above it a cavity (his "secondary cavity") which is roofed over by a bridge of cells from the "Deckschicht," or, as he calls it, the "outer layer." The history of the structure, as he gives it, is briefly this. The blastodermic vesicle consists of a closed sac of flattened cells, the outer layer, and of a mass of rounded cells within at one pole, the inner mass. The latter differentiates into two parts, which become ectoderm and entoderm. The ectoderm becomes continuous at its margin with the outer layer, from which it is separated over its central area by a shallow cavity. The ectoderm increases in extent and becomes somewhat cup-shaped, so that the cavity increases in depth, but it is filled with amœboid cells derived from the outer layer. Later the ectoderm of the disk flattens out, and the cells of the outer layer above it fuse with it and become a part of the true germinal ectoderm. The interpretation which Heape puts on these phenomena is, that they are a transitory representation of the inversion of the germinal layers which is carried to such a great extent in some rodents. I see no reason why Heape's observations and conclusions are not entirely correct. A similar phenomenon has been figured by Hubrecht ('89, Plate XVI.) in the hedgehog. Here, however, the portion of the outer layer, or "trophoblast," which is separated from the germinal disk ectoderm, does not become fused with the disk later, but remains in contact with the uterine mucosa. This roof-like structure, where it comes in contact with the ectoderm of the disk, is clearly continuous with the cells of the "trophoblast" and also with those of the disk, so that Hubrecht's ('89) Fig. 20 B, Plate XVI., resembles my figures of sections through the posterior attachment of the bridge in the pig.

The condition in the pig, although it seems at a casual glance to resemble the structure in the mole embryo, is not directly comparable with it. In the first place, the structure in the mole forms from the beginning an uninterrupted covering to the ectoderm of the germinal disk, and continues to do so through the subsequent development, up to its complete obliteration through fusion with the disk. During the whole process no stage occurs where there is any trace of an *overgrowth*, such as I have found in the pig, or of an external opening into the cavity which lies between the two layers in question. Moreover, this cavity in the mole is largely filled with a loosely arranged mass of amœboid cells, except in one case, where, as Heape ('83, Plate XXIX. Fig. 25) says, their absence is due to mechanical injury in the process of preparing the sections. Furthermore, it may be noted that this bridge-like structure appears at a much earlier ontogenetic stage in the mole than in the pig. In the former the entoderm covers the area of the germinal disk only; in the latter I find a complete didermic vesicle when the first trace of the bridge cells appears. It is true, we need not be surprised to find an inversion of the layers in other mammals than those in which it has already been established, especially in the light of Mall's ('93) paper on a human embryo of the second week, in which he explains the conditions as the result of inversion; but, for the reasons I have given, I do not consider the bridge in the pig as even a potential inversion, — the less so as the explanation I am about to offer is to my mind a much more satisfactory interpretation of the phenomena. If it should be urged that the bridge is homologous with the roof-like structure over the germinal disk of the hedgehog (Hubrecht '89), it would be necessary to assume the existence of a potential opening through this structure into the cavity beneath it from the very beginning of its formation, but the facts, as recorded for the hedgehog, seem to furnish no grounds for this assumption. Moreover, in this animal the roof-like structure never comes in contact with the ectoderm of the germinal disk, but contributes to the formation of the placenta, a very different fate from that of the bridge in the pig.

I am inclined to compare this bridge with the overgrowth which occurs in the development of Amphioxus just after gastrulation and the elongation of the embryo have taken place. We know through the investigations of Kowalevsky ('67 and '76) and of Hatschek ('81) that at this time there is a sinking of both ectoderm and entoderm along one side of the gastrula, the future dorsal or neural side of the animal, which forms the so called medullary plate, and at about the same time a proliferation of cells begins at the posterior margin of the blastopore, and, growing forward over the blastopore and the medullary plate, meets lateral elevations on either side, and fusing with them forms a continuous roof over the dorsal depression, with an opening at the anterior end, which persists for a considerable time as the neuropore. The neural tube is later formed from the medullary plate, which is in this way cut off from the rest of the ectoderm, but the overgrowth itself takes no part in the formation of the tube, as we see clearly from Kowalevsky's ('76) Figs. 11, 12, and 13, Taf. XV., where the cells of the medullary plate grow across under the roof, and thus separate the roof from the lumen of the neural tube. Kowalevsky says on this point: "Die Rückenrinne, obgleich von aussen vollständig bedeckt, innen — unter der Haut — noch offen ist. Die Querschnitte der Gastrula und der zuletzt angeführte Querschnitt auf der Fig. 11 erklären uns diese Erscheinung ganz einfach. Querschnitte der etwas weiter ausgebildeten Larve, Figg. 12 u. 13 zeigen uns nun, dass die oberen Ränder der Medullarplatten sich bald verbinden, anfangs vermittelst einer sehr feinen und platten Brücke, welche sich aber bei den weiter ausgebildeten Larven bedeutend verdickt und so ein Verhältniss annimmt, wie bei dem ausgewachsenen Amphioxus."

Now the development of the bridge in Sus scrofa domesticus, as I have traced it in the present paper, corresponds in many important points with the development of the dorsal overgrowth in Amphioxus. In the first place, it begins by a marked proliferation of cells at one pole of the chief axis of the germinal disk, and at the same time by a slight elevation laterally on either side of this axis and nearer the opposite pole. The median growth is more rapid than the lateral growths, and gives a condition like that of Fig. 1, Plate I., which is much the same as that figured by Kowalevsky ('76, Taf. XV. Fig. 3) and by Hatschek ('81, Taf. III. Fig. 37) for Amphioxus. The overgrowth continues in the direction of the median axis, and the three parts fuse to form the continuous bridge, as already described for the subsequent stages, represented by the figures on Plate I. These correspond with the phenomena as they have been described by Kowalevsky in Amphioxus: "Die jetzt beginnende Schliessung der Rückenfurche geht hier, so wie bei den anderen Wirbelthieren, von hinten aus, wobei die ganz hinteren Ränder, welche die Einstülpungsöffnung rückwärts begrenzten, sich aufheben, eine Art Dach über diese Oeffnung bilden und immer mehr und mehr nach vorne wachsend und mit den seitlichen Rändern der Rückenfurche verschmelzend den Rücken, resp. das Nervenrohr, zu bilden beginnen."

It is for these reasons that I have oriented my embryos in the way already described. The opening into the depression below the bridge corresponds, I believe, to the neuropore of Amphioxus, and I am inclined to carry the homology of the two forms still further, and suggest that the canal which I have shown in Fig. 20, Plate IV., corresponds to part of the neurenteric canal of Amphioxus.

There are several objections to this theory which suggest themselves at once. In the first place, as to the structure of the two overgrowths; that in Amphioxus is figured as consisting of but one layer of ectodermal cells; the bridge in the pig, on the contrary, is *from two to three layers of cells thick.* This seems to me but a minor point, however, readily explained by the morphological differences between the larva of Amphioxus and the blastodermic vesicle of the Mammalia. In the former case there is no part which may not be said to develop directly into some important tissue or organ of the adult animal; in the latter, it is essentially the germinal disk only of which this is true. Here, then, we have a germinal and an extra-germinal region, and in the process of rapidly increasing the number of cells in the disk the extra-germinal cells of the ectoderm, as well as the cells of the disk, apparently contribute to the development of the bridge, thus producing an overgrowth two or three cells thick. Again, it may be urged that I have not shown a blastopore around which the overgrowth should take place. I have found in my youngest embryos no trace of an opening through the germinal disk which could be compared with what Hertwig ('93) says may possibly be a blastopore, as figured by Heape ('83), Selenka ('86–'87), and Keibel ('89). But the blastopore in Amphioxus becomes the neurenteric canal, which leads from the posterior end of the cavity beneath the overgrowth into the gastrula cavity. It is at just this point in several of my embryos that I find a canal leading from the cavity beneath the bridge to the cavity located at the margin of the disk, between ectoderm and entoderm. To be a true neurenteric canal, it should be continued into the gastrula cavity, i. e. the cavity within the entoderm; but on account of the loose connection of the entodermal cells, it is impossible here to trace any such passage. I do not, however, think we should be justified in asserting on this account that it does not exist. There ought, however, to be at least a fusion of the two primary germ layers in this region, such as always occurs, I believe, in the case of a true neurenteric canal.

Still another objection may be raised to this theory, and that is the extremely remote relationship existing between Amphioxus and the Mammalia. If the bridge of the pig is really a reappearance of a structure which occurs as far back in phylogeny as the lowest representative of the Vertebrata, why may we not justly look for its presence in intermediate groups? The question is certainly a fair one, and I can only say that, so far as I am aware, no structure having so marked a resemblance to the overgrowth in Amphioxus has been recorded in any intermediate group. I am tempted, however, to call attention here to a parallel case. The early cleavage in mammals, as described especially by Tafani ('89), bears a striking resemblance to the early cleavage of Amphioxus. Why, then, do we not find the same type of cleavage occurring in intermediate groups of vertebrates? Here again it must be admitted that we do not find it, but in this case the reason is plain; it is because the whole structure of the ovum is so changed by the accumulation in it of nutrient material, that cleavage on the type of Amphioxus is impossible, and it is not until we reach the Mammalia that the conditions are such as to admit of total equal cleavage. But is it not for the same reason that the steps which lead up to the formation of the neural tube have been modified, and that the overgrowth in Amphioxus finds its first striking recurrence in the mammalian embryo? The lumen of the canal is often extremely small in other mammals, and has in some cases been represented by a single line, e. g. Robinson ('92, Plate XXIII. Fig. 13 A, Plate XXIV. Fig. 15 D, and Plate XXVI. Fig. 17).

A more serious objection exists in the fact that the cavity beneath the overgrowth in Amphioxus becomes the neural canal, whereas, as I have traced it in the pig, it becomes obliterated by a fusion of the bridge with the ectoderm of the disk. I would not be understood as considering the canal which I have compared to the neurenteric canal decisive evidence in favor of this theory; it is, however, a significant phenomenon occurring in a significant position. To my mind it occupies the position of the neurenteric canal in Amphioxus; that it is certainly the neurenteric canal of the pig, I would not presume to say; the descriptions of this canal in mammals are varied; the bridge and canal which I have described have never before been recorded in the Mammalia, so far as I am aware.

3. *Summary.*

My conclusions as to this bridge may be briefly summarized as follows. Two interpretations of the structure have presented themselves as in some measure probable. The first homologizes it with the thickening of the "Deckschicht" or Rauber's layer, or, as Heape ('83) calls it in the mole, the outer layer, which through the development of a secondary cavity becomes separated from the true ectoderm of the germinal disk and forms a sort of roof over it. That this structure is not homologous with the bridge seems to me evident from the fact that in the case of the bridge there is always an opening leading from the outside into the cavity beneath the bridge, and this cavity is never filled with amœboid cells as is the cavity in the mole. Furthermore, on the bridge there are found in some cases "Deckzellen," — or rather their remains, consisting of homogeneously staining nuclei and little cytoplasm, — which clearly can take no part in the formation of either bridge cells or true ectodermal cells. Again, the roof of overlying cells in the mole makes its appearance and finally fuses with the germinal disk ectoderm at an earlier stage in ontogeny than that at which the bridge in the pig develops.

The second theory, which seems to me the more probable, homologizes the bridge with the overgrowth along the dorsal side of Amphioxus. The reasons for this comparison are that the two structures develop at about the same time in ontogeny in the two cases, i. e. just after the formation of a didermic vesicle; that, further, a process of growth can be traced for the bridge which corresponds closely to the method of growth in the case of the structure under consideration in Amphioxus; and, finally, that there is a median thickening of the germinal disk corresponding topographically to the medullary plate of Amphioxus, a free margin to the bridge corresponding to the neuropore, and a canal at the opposite pole which may, perhaps, be compared with the neurenteric canal of the primitive vertebrate. From my present knowledge of the bridge in the pig, I cannot homologize it with the roof-like structures in the shrew and the mole, and if it is not comparable with the overgrowth in Amphioxus, it seems to me necessary to regard it as a structure hitherto undescribed in vertebrate embryology. Whatever the interpretation of the bridge may be, we have the fact of its existence, and it is reasonable to expect that it will be found in other mammals as well, as, for example, in the sheep, in which the immediately succeeding stages of development are so similar to those of the pig.

I wish to express my thanks to Dr. Alexander Agassiz, to whom I am greatly indebted for the opportunity of studying at his private laboratory at Newport and for the privilege of using his library, and to Dr. E. L. Mark, who has very kindly followed all my work and examined my preparations with great care, and also to the employees of the abattoir, who have given me much assistance in securing material.

CAMBRIDGE, April 18, 1894.

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EXPLANATION OF PLATES.

All the drawings were made with the camera lucida directly from the object itself, with the exception of Fig. 2, Plate I., which is a graphic reconstruction made from sections drawn with the camera. In the case of all transverse sections it is the *posterior* face of the section that is shown, so that right on the figure corresponds to the right side of the disk. The embryos came from four uteri, and may accordingly be grouped as follows: A, Figs. 1, 3, 4, 10, 27; B, Figs. 2, 21, 22, 23, 26; C, Figs. 5, 6, 14–20, 24, 25; D, Figs. 7, 8, 9, 11, 12, 13.

PLATE I.

All figures magnified 100 diameters, and oriented on the plate with the chief axis vertical and the anterior pole towards the top.

Figure 1. A portion of the blastodermic vesicle containing the germinal disk. The posterior overgrowth is marked, and the marginal elevations and median depression are apparent.

" 2. A later stage than the preceding, with the posterior and the lateral overgrowths fused at two points.

" 3. One continuous overgrowth or bridge, with no trace remaining of the fusion of parts.

" 4. A later stage showing a more extensive bridge with a lateral opening at the right, where the lateral and the posterior overgrowths have not completely fused.

" 5. A germinal disk with ovate outline and highly developed bridge. The broad end of the disk is anterior.

" 6. Enlarged disk, ovate, with no separate bridge. Sections show that the bridge has fused with the ectoderm of the disk.

WYSSE. BLASTODERMIC VESICLE. PLATE I.

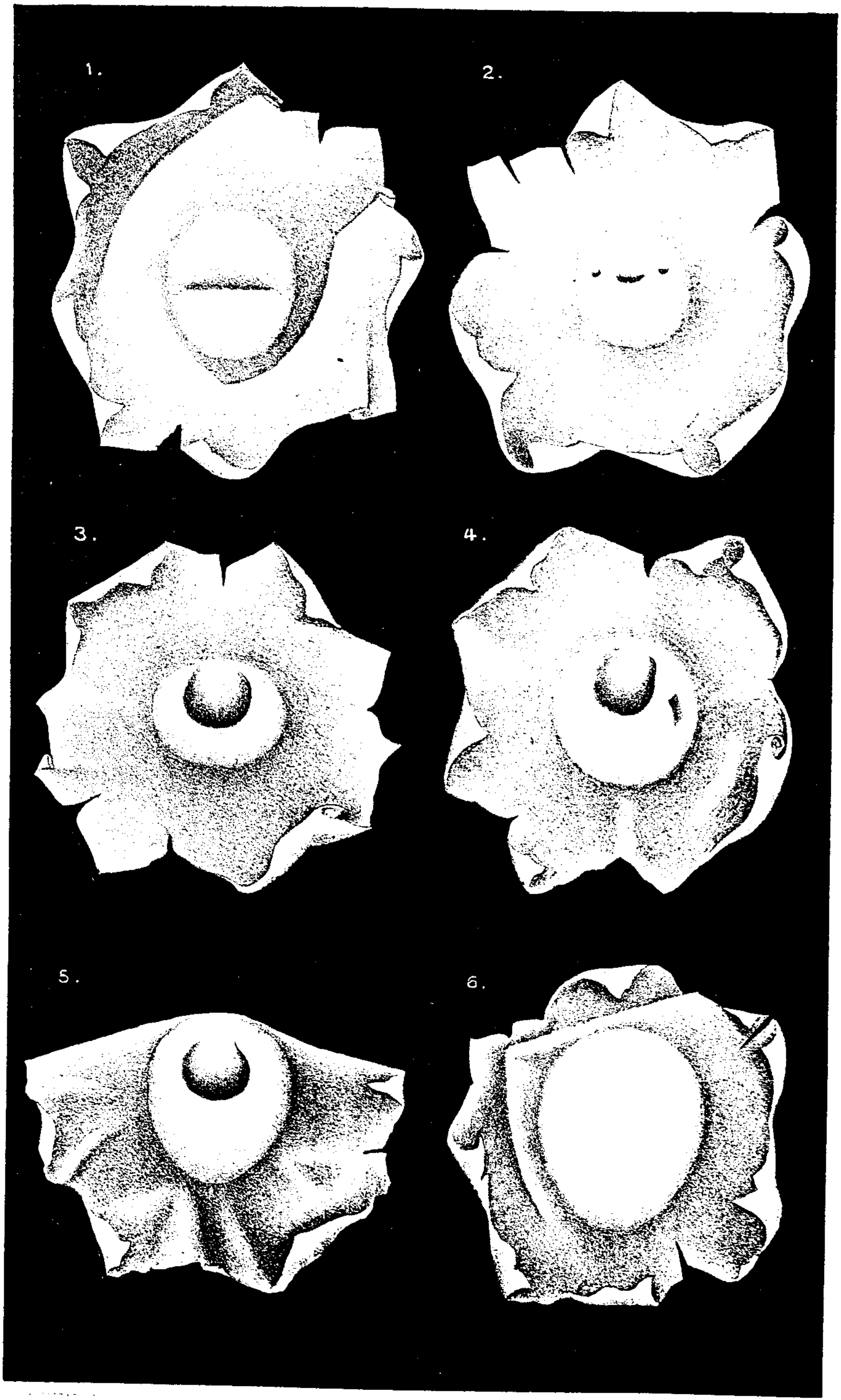

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PLATE II.

All figures magnified 400 diameters, ectoderm uppermost.

Figure 7. Transverse section of a very young germinal disk, showing one cell at the centre projecting above the general level of the ectoderm, but clearly an ectodermal cell.

" 8. Section immediately succeeding that of Fig. 7, and showing essentially the same phenomena.

" 9. More anterior section of the same disk showing the even surface of the ectoderm and the general arrangement of the cells. No "Deckschicht" cells.

" 10. Longitudinal section, nearly median, through the germinal disk of Fig. 1. At the left hand or posterior end is seen an early stage in the development of the bridge, which here consists of two layers of cells, the outermost resembling the extra-germinal ectoderm, the inner the germinal ectoderm. Note the dividing nucleus at the base of the bridge.

" 11. A nearly median longitudinal section of another germinal disk in a little later stage of development.

" 12. More lateral section through the same embryo as Fig. 11, showing lateral continuity of the bridge and the cavity beneath it.

" 13. A still more lateral section of the same disk as the two preceding, in which the cavity has disappeared, but the bridge cells are readily distinguished from the true ectodermal cells of the disk.

WEYSSE-BLASTODERMIC VESICLE. PLATE II.

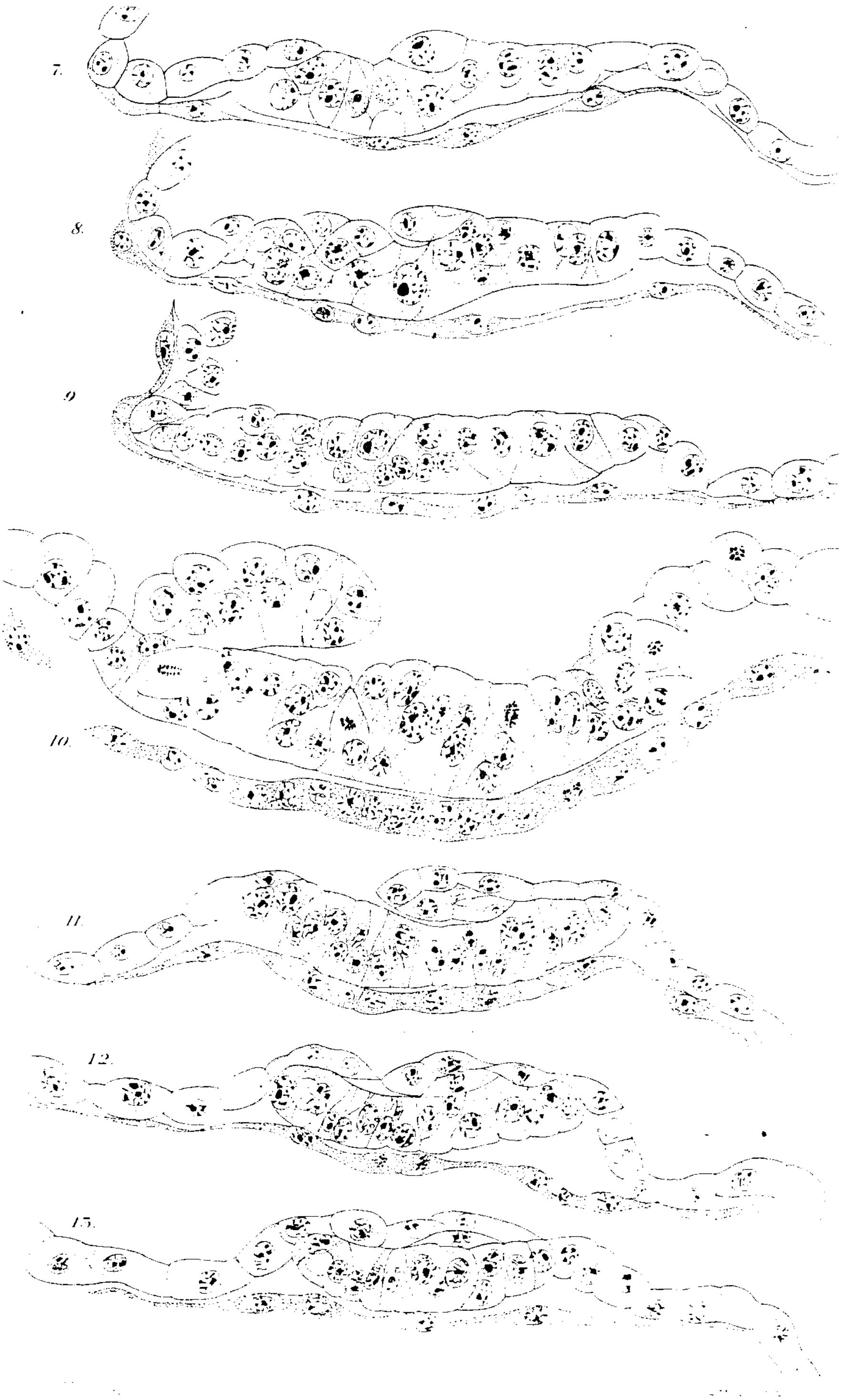
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PLATE III.

All figures magnified 400 diameters, and all drawn from longitudinal sections through the germinal disk of Fig. 5. The anterior end is at the right.

Figure 14. First section of the disk; the disk cells first appear near the anterior end on account of the ovate outline of the disk.

" 15. Second section in the series; merely shows an extension of the germinal-disk ectoderm.

" 16. Fourth section. First appearance of the bridge, marked off by a distinct cavity.

" 17. Sixth section through the disk. Extension of the cavity and decrease in thickness of the bridge.

" 18. Seventh section, showing free margin of the bridge at the anterior end, with posterior attachment.

" 19. Eighth or median section; here we have the most posterior point of the free margin of the bridge. The cavity beneath extends a short distance towards the posterior pole, between the cells.

WEYSSE: BLASTODERMIC VESICLE. PLATE II.

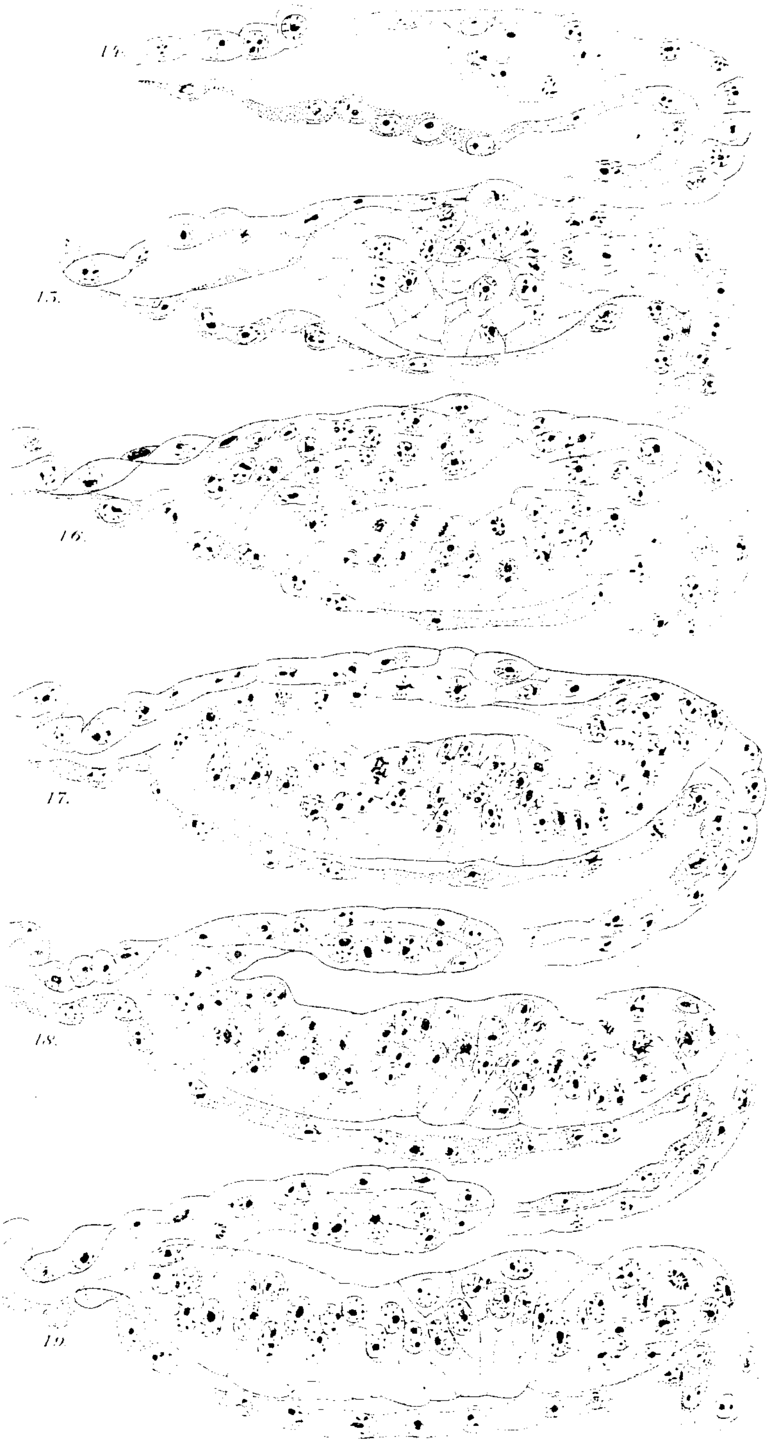
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PLATE IV.

Figures 20 and 27 magnified 400 diameters, all others 275 diameters. Ectoderm in every case uppermost.

Figure 20. The ninth section in the same series as those of Plate III. The free margin of the bridge is again nearer the anterior pole, while the cavity beneath extends by a narrow canal completely through the ectoderm of the disk into the extra-germinal space between ectoderm and entoderm.

" 21. Somewhat oblique longitudinal section nearly through the centre of Fig. 2, Plate I. The ectoderm of the disk is greatly thickened, the cavity beneath the bridge is rather shallow, but there is a marked depression just in front of the free edge of the bridge. The entoderm is thickened beyond the area of the disk in the extra-embryonic region.

" 22. A nearly transverse section through a much older germinal disk, which shows the decrease in thickness of the ectoderm attending an extension in area and the fusion of the bridge along the median portion.

" 23. A slightly more anterior section of the same disk as Fig. 22, where we see at the left lateral margin the fusion of the bridge not quite completed.

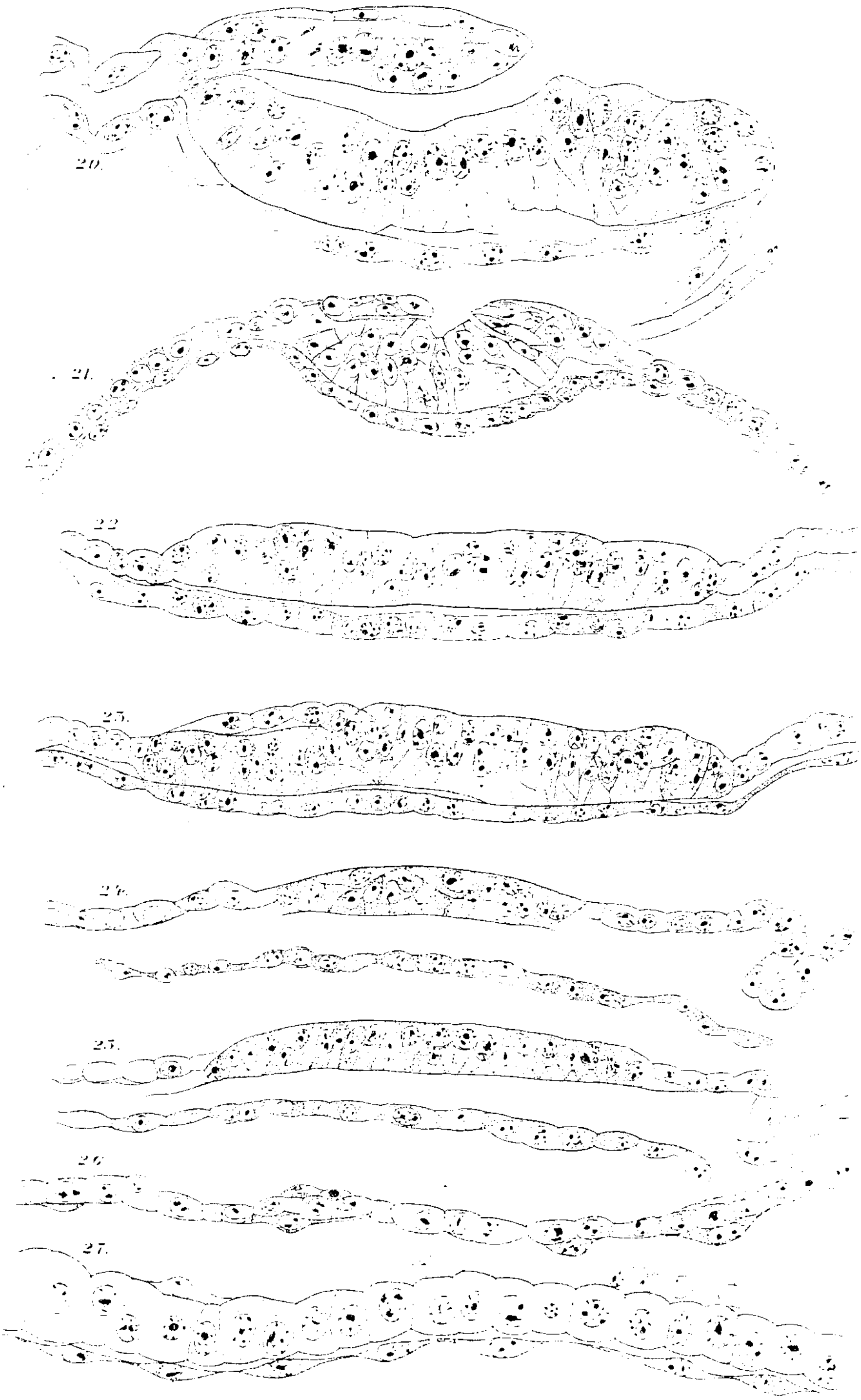
" 24. Transverse section, the fourth from the anterior end of the germinal disk of Fig. 6, showing the bridge cells in contact with the germinal-disk ectoderm.

" 25. Seventh section of same disk as the preceding, showing near the median line the last trace of the fusion of two bridge cells with the ectoderm.

" 26. Section through the extra-germinal region of the blastodermic vesicle of Fig. 2, Plate I. On the upper side are a few "Deckschicht" cells, flattened and disintegrating; then a layer of typical ectodermal cells, and, below, the normally distributed entodermal cells of this stage.

" 27. Section through the extra-germinal region of Fig. 3, Plate I. The "Deckschicht" cells are more numerous than in the preceding case, and at one point several are in contact with one another, — an unusual condition. The entodermal cells are more numerous than in the preceding, since this is a later stage of development.

WEYSSE—BLASTODERMIC VESICLE. PLATE V.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XIII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON TERNARY MIXTURES.

FIRST PAPER.

By Wilder D. Bancroft.

Presented by C. L. Jackson, May 9, 1894.

Following out the analogy between dissolved substances and gases, Nernst deduces the law that, when two dissolved substances have no common ion and do not react chemically, the influence of each on the solubility of the other is zero, within certain undefined limits. He says:* "Die Analogie zwischen der Auflösung und Sublimation bezw. Dissociation fester Stoffe zeigt sich nun auch deutlich ausgesprochen, was den Einfluss fremden Zusatzes betrifft. Ebenso wenig wie die Sublimationsspannung bei Gegenwart fremder indifferenter Gase sich ändert, wird die Loslichkeit eines festen Stoffes durch Zusatz eines zweiten (in nicht zu grosser Menge) beeinflusst, wofern der hinzugefügte fremde Stoff nicht chemisch auf jenen einwirkt; und ebenso wie die Dissociationsspannung im höchsten Maasse durch Zusatz eines der gasförmigen Zersetzungsproducte beeinflusst wird, so variirt entsprechend auch die Löslichkeit derjenigen Stoffe, bei welchen die Auflösung mit einem mehr oder weniger vollständigen Zerfall verbunden ist, die also bei ihrer Auflösung mehrere Molekülgattungen liefern, wenn eine dieser letzteren der Lösung hinzugefügt wird." There are several things in this statement which are open to criticism. If taken literally, the author implies a fundamental difference between solutions of liquids in liquids, and solids in liquids, a distinction which is not in accordance with the view that in dilute solutions the solute,† whether liquid or solid in the pure state, behaves like a gas at that temperature. If applied to any dissolved substance, the statement just quoted is too inaccurate to need any comment. The precipitation of salts by alcohol is a well known instance where it does not apply, and, in general, adding to a solution a substance in which the solute is practically insoluble diminishes the solubility of the latter. This is recognized by Nernst, for he has based a method for determining reacting weights upon it.* Even if limited to solids, the proposition cannot be admitted. We have the precipitation of lactones by potassium carbonate as an intermediate step, and the precipitation of salts by phenol as a definite case of diminished solubility without the presence of a common ion. Other cases could be cited, if necessary, and there are also examples where an increase of solubility takes place when a solid substance is added to a solution containing another solid as solute. The explanation usually offered under these circumstances is, that "double molecules" are formed, a mode of getting round the facts which is not always entirely satisfactory.

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* Theor. Chemie, p. 383.

† There seems to me a need for a word denoting the dissolved substance. In future I shall use the word "solute," meaning the substance dissolved in the solvent. Instead of the phrase "infinitely miscible liquids," I propose "consolute" liquids.

Since in the application of the gas laws to solutions there has been observed no difference between a solid and a liquid when dissolved, I am inclined to think that the general statement should be, that in all cases where a third substance, *B*, is added to a solution of *A* in *S*, the solubility of *A* undergoes a change. This variation may be large or small, positive or negative, depending on the nature of the three substances *A*, *B*, and *S*. When both *A* and *B* are liquids, or even when only one of them is, the effect is so marked as to be familiar to all; when both are solids, the effect is not yet recognized by so competent an authority as Nernst.

The work of the last few years on solutions has been devoted to bringing out the analogy between the dissolved substance and gases. In the cases of changed solubility, no common ion being present, the analogy is no longer with gases, but with liquids. The added substance acts as a liquid, precipitating the solute more or less in proportion as the dissolved substance happens to be more or less soluble in it. The laws governing these displacements are entirely unknown, with the exception of Nernst's Distribution Law,† which is only a first approximation, in that it takes no account of the changing mutual solubilities of the hypothetically non-miscible liquids. Under these circumstances it seemed to me desirable to investigate the laws governing systems composed of three substances, and the experiments which I communicate in this paper have been made on the simplest form of ternary mixtures, that where all three substances are liquids. The subject has been very little studied, the only researches known to me being by Tuchschmidt and Follenius,* Berthelot and Jungfleisch,† Duclaux, ‡ Nernst, § and Pfeiffer. ‖ Of these, all except the first and last deal with the equilibrium between two liquid phases; the paper of Tuchschmidt and Follenius contains but one series of measurements, while Pfeiffer remarks, apropos of his own extended investigations, that "there is very little to be made out of them." In this he does himself an injustice, for, as I shall show, his results are very satisfactory and astonishingly accurate when one remembers how they were made.

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* Zeitschr. f. ph. Chem., VI. 16. 1890.

† Teilingssatz.

The simplest case of three-liquid systems is when one has two practically non-miscible liquids, and a third with which each of the others is miscible in all proportions; for then any complication due to the mutual solubility of the two dissolved liquids is avoided. It is possible to say something *a priori* about the law which governs these saturated solutions. Let A and B be two non-miscible liquids, S the common solvent with which A and B are miscible in all proportions when taken singly, and let the quantity of S remain constant, so that we are considering the amounts of A and B, namely x and y, which will dissolve simultaneously in a fixed amount of S. It is known, experimentally, that the presence of A decreases the solubility of B, and *vice versa;* it is required to find the law governing this change of solubility. This, being a case of equilibrium, must come under the general equation of equilibrium.

$$(1) \qquad \frac{\delta F(x, y)}{\delta x} dx + \frac{\delta F(x, y)}{\delta y} dy = 0,$$

where dx and dy denote the changes in the concentrations of A and B respectively.

This equation, though absolutely accurate, is of no value practically so long as the differential coefficients are unknown functions. In regard to them we may make two assumptions. The decrease in the solubility of A may be proportional to the amount of B added, and independent of the amounts of A and B already present in the solution. The differential equation expressing this is:

$$(2) \qquad a\,dx + b\,y = 0,$$

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* B. B., IV. 583. 1871.

† Ann. chim. phys., [4.], XXVI. 396. 1872.

‡ Ibid., [5.], p. 264. 1876.

§ Zeitschr. f. ph. Chem., VI. 16. 1890.

‖ Ibid., IX. 469. 1892.

where a and b are proportionality factors and constants. This equation may be rejected on *a priori* grounds, because it does not show that when B is absent, the miscibility of A with S is infinite, and also because it has no similarity with the other equations representing chemical equilibrium. The second assumption is that the change in solubility may be a function of the amounts of A and B already present. This is the usual condition of chemical equilibrium, and is known as the Mass Law. Its mathematical expression is

$$\frac{\alpha\, d\, x}{x} + \frac{\beta\, d\, y}{y} = 0, \text{ or}$$

$$\alpha\, d \log x + \beta\, d \log y = 0, \tag{3}$$

where x and y denote the amounts of A and B in a constant quantity of S, α and β are proportionality factors, and the logarithms are natural logarithms.

If α and β are constants, this equation is integrable, and gives when cleared of logarithms:

$$x^{\alpha}\, y^{\beta} = \text{Constant.} \tag{4}$$

If we make $\frac{\alpha}{\beta} = n$, we shall have:

$$x^{n}\, y = C, \tag{5}$$

where C is of course different in value from the constant in equation (4).

Before we proceed to test equation (5) experimentally, it remains to be seen in what unit x and y should be expressed. It is obvious that the nature of the unit has no effect on the general form of the equation, nor upon the exponential factor n. The only change will be in the value of the integration constant $\log C$, so that the measurements may be expressed in any form that is convenient, as chemical units,* for example, grams per litre, volumes, reacting volumes, or anything else. It is not even necessary that x and y be expressed in the same unit, though it would probably always be more practical. In my own experiments x and y are expressed in cubic centimeters because they were measured directly as such, and in this way it was not necessary to make determinations of the densities of the liquids used, nor any assumptions in regard to their reacting weights. Equation (5) will not remain unchanged if the reacting weight of A or B varies, that is, if the ratio of the active mass to the actual mass changes as x or y changes. The converse of this is also true, that if the system follows the law $x^n y = C$, the common solvent remaining constant, the reacting weights of the substances A and B cannot have varied with the concentration.

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* I have adopted the following nomenclature for molecular and atomic weights, viz. reacting and combining weights. As the reacting weight is proportional to the chemical unit experimentally, I propose that the gram molecule in the unit of volume (reacting weight in grams per litre) be called the chemical unit, or simply the unit. The object of these arbitrary changes in our chemical terms is to do away with everything involving or implying the assumption of the existence of molecules and atoms.

I have found that the equation, $x^a y^3 =$ Constant, is the expression representing the saturated solutions of two non-miscible liquids in a constant quantity of a consolute liquid. I find, however, that in most cases the concentrations cannot be given by one curve, but involve two, so that for one set of concentrations I have the relation $x^{n_1} y = C_1$, for the other set $x^{n_2} y = C_2$. This cannot be true unless the two sets of saturated solutions correspond to different conditions. This is the case. Duclaux* found that a saturated solution of amylalcohol and water in ethylalcohol became turbid on adding a drop either of amylalcohol or of water. In other words the solution was sensitive to an excess of either liquid.† I have confirmed this result, and it is perfectly general. It is not proper, however, to draw the conclusion that the solution is saturated in respect to both liquids. If to a given saturated solution of chloroform, water, and alcohol, for instance, one adds a drop of water or of chloroform, the solution becomes turbid; but what separates out is the same in both cases. It is analogous to a saturated solution of salt in a mixture of alcohol and water. It is indifferent whether one adds alcohol or salt to the solution. In either case, there is a precipitate; but in both cases the precipitate is salt, and the solution is saturated in respect to salt, not in respect to alcohol. It is not so easy to see what takes place in a system composed of liquids because the precipitate, being itself a liquid, dissolves part of the solution, and the new phase is not composed of pure substance. This need not trouble us, for, theoretically at any rate, the precipitate may be treated as pure liquid, and the final equilibrium looked upon as due to a subsequent reaction. One of the two curves represents, then, the set of solutions which is saturated in respect to chloroform, and not in respect to water. Whether one adds water or chloroform, to these solutions, the precipitate is chloroform. The other curve represents the mixtures which are saturated in respect to water, and not in respect to chloroform. Either water or chloroform, when added to these solutions, produces a precipitate of water. These two sets of solutions are easily distinguishable qualitatively, because in the first case the new phase, containing a large percentage of chloroform, is denser than the mixture from which it separates, while in the second case the new phase, containing chiefly water, is lighter than the original solution. The point where the new phase changes from being denser to being lighter than the first phase is the point of intersection of the two curves. At this point only is the nature of the precipitate determined by the nature of the infinitely small excess added. The intersecting point represents the concentration at which, were chloroform and water solids at that temperature, both could be in equilibrium with the solution and its saturated vapor. It corresponds to the concentration of a solution containing two salts with a common ion which is in equilibrium with the two solid salts, formation of a double salt being excluded. In one respect the analogy between a system having three liquid components and one composed of two solids and a liquid does not hold. If to a saturated solution of silver bromate silver acetate is added, the precipitate is silver bromate, and, conversely, the precipitate is silver acetate if silver bromate be added to a saturated solution of silver acetate. The salt with the less concentration precipitates the one with the greater, up to a certain point. In a chloroform-water-alcohol mixture in which chloroform is present in large quantities, the precipitate is water, or the substance with the greater precipitates the one with the lesser concentration. This difference of behavior is due to the new phase being a solid in the one case and a liquid in the other. By a suitable choice of the three components, and by varying the temperature, the substance in respect to which the solution was saturated could be made to separate either as a liquid or a solid phase, and this difference could be made zero. The transition point would come when the equilibrium was between four phases, one solid, two liquid, and one gaseous.

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* Ann. chim. phys., [5.], VII. 264. 1876.

† Ostwald, Lehrbuch, I. 819.

There is no apparent theoretical reason why the two curves should not be prolonged beyond their intersection; but there is a very good practical one. Beyond the point of intersection the curves denote saturated but labile solutions, and a supersaturated system composed of liquids is almost impossible to realize. When I come to the study of ternary mixtures having one or more solid components, I hope to be able to follow one of the curves at least beyond the intersecting point; but in the present work I have made no such attempt.

I will now describe the method used in my work, and then take up the experimental data obtained. As pairs of non-miscible liquids, I have taken chloroform and water, benzol and water; and as consolute liquids, ethylalcohol, methylalcohol, and acetone. The next point was how to determine the composition of the saturated solutions. The methods of quantitative analysis are useless in this case; but the problem is solved without difficulty by quantitative synthesis. Instead of making a saturated solution and analyzing it, I measured the quantities required to make a saturated solution at the required temperature. Definite amounts of the consolute liquids were put in test tubes by means of a carefully graduated pipette; varying quantities of one of the non-miscible liquids were run in from a burette, and the second non-miscible liquid added from another burette to saturation. The test tubes were corked, warmed just above the temperature at which the final readings were made, so that there should be a single homogeneous liquid layer, and placed in a constant temperature bath. If the tube clouds, it is beyond the saturation point; if it remains clear, it is not up to it, the required value lying between the two. By making a series of experiments one can bring the limiting values very close together, and thus determine the saturation point with great accuracy. The constant temperature bath was at 20° C. No correction was made for the amounts of the three liquids evaporating off into the vapor space in the upper part of the test tubes; but by using different sized test tubes this space did not vary much, being about five cubic centimeters, so that the error due to this may be neglected.

The chloroform used (Squibb's) was treated with sodium bisulphite solution to free it from acetone, washed thoroughly with water, dried over calcium chloride and fractionated, twelve hundred grams going over within one quarter of a degree. Kahlbaum's crystallized benzol was recrystallized twice and fractionated to constant boiling point. The ethylalcohol was dried over lime and copper sulphate and fractionated. The lot used distilled within half a degree. Part of the acetone (from Eimer and Amend) was converted into the bisulphite compound, back again, dried over potassium carbonate and calcium chloride, and fractionated. Another portion was treated direct with calcium chloride and fractionated. I could detect no difference between the two lots. I tried to purify a sample of acetone from Cutler Brothers, purporting to be manufactured by Merck in Darmstadt; but it was so bad that I used none of it in my experiments. The methylalcohol (from Kahlbaum) was dried over anhydrous copper sulphate and fractionated.

The measurements in the tables are the mean of at least four determinations, and the error is probably not more than 5% except in the cases where the quantity of one component is less than 0.20 c.c., when it may easily rise to 10%. The values for n are accurate to within 2% without much question. The values for log C are more untrustworthy, being much affected by a slight variation in n, while the term C is liable to even greater fluctuations, and is not given, as being too uncertain. Under the headings "Calc." are the values required by the formula to correspond with the experimental data for the other component. The figures in the column marked log C are Briggsian logarithms. As will be noticed, I have not always taken the mathematical mean of this column as the value of log C in the formula. It seemed better to take the value which best satisfied the experimental data, and to ignore numbers which were obviously faulty.

TABLE I.

x c.c. H_2O; y c.c. $CHCl_3$; 5 c.c. Alcohol. Temp. 20°.

Formula $x^{n_1} y = C_1$; $n_1 = 1.90$; log $C_1 = 1.190$.

Water.		$CHCl_3$		
Calc.	Found.	Calc.	Found.	log C_1.
9.94	10.00	0.195	0.20–	1.195
8.99	9.00	0.24	0.24	1.192
7.98	8.00	0.30	0.30	1.193
7.14	7.00	0.385	0.37	1.174
6.00	6.00	0.515	0.515	1.190
5.00	5.00	0.73	0.73	1.191
3.97	4.00	1.12	1.13	1.197
			Average,	1.190

Formula $x y^{n_2} = C_2$; $n_2 = 1.111$; log $C_2 = 0.742$.

				log C_2.
3.00	3.00	1.73	1.73	0.741
1.99	2.00	2.49	2.51	0.745
1.01	1.00	4.66	4.60	0.737
0.92	0.91	5.07	5.00	0.736
0.755	0.76	5.96	6.00	0.745
0.635	0.63	7.06	7.00	0.738
0.55	0.55	8.00	8.00	0.743
0.48	0.49	8.86	9.00	0.750
0.43–	0.425	10.06	10.00	0.739
0.20	0.20–	20.00	20.00	0.742
0.127	0.125	30.24	30.00	0.738
			Average,	0.741

TABLE II.

x c.c. Water; y c.c. $CHCl_3$; 5 c.c. Methyl Alcohol. Temp. 20°.
Formula $x^{n_1}y = C_1$; $n_1 = 2.30$; $\log C_1 = 1.291$.

Water.		$CHCl_3$.		
Calc.	Found.	Calc.	Found.	log C_1.
9.91	10.00	0.10	0.10	1.300
5.01	5.00	0.48	0.48	1.288
4.03	4.00	0.81	0.80	1.283
1.99	2.00	3.97	4.00	1.294
			Average,	1.291

Formula $x^{n_2}y = C_2$; $n_2 = 1.25$; $\log C_2 = 1.061$.

				log C_2.
1.49	1.49	7.00	7.00	1.061
1.34	1.35	7.93	8.00	1.065
1.12	1.12	10.00	10.00	1.061
			Average,	1.062

TABLE III.

x c.c. Water; y c.c. Chloroform; 5 c.c. Acetone. Temp. 20°.
Formula $x^{n_1}y = C_1$; $n_1 = 1.415$; $\log C_1 = 0.194$.

Water.		Chloroform.		
Calc.	Found.	Calc.	Found.	log C.
5.01	5.00	0.16	0.16	0.193
4.00	4.00	0.22	0.22	0.194
3.47	3.50	0.266	0.27	0.201
3.00	3.00	0.33	0.33	0.193
2.49	2.50	0.43	0.43	0.196
2.01	2.00	0.586	0.58	0.189
			Average,	0.194
	1.50		0.74	
	1.20		0.83	
	1.00		0.955	
	0.93		1.00	
	0.79		1.12	
	0.71		1.20	
	0.58		1.40	
	0.53		1.50	
	0.505		1.60	
	0.38		2.00	
	0.30–		2.50	
	0.25		3.00	
	0.21		3.50	
	0.19		4.00	
	0.16		5.00	
	0.12		10.00	

TABLE IV.

x c.c. Water; y c.c. Benzol; 5 c.c. Alcohol. Temp. 20°.

Formula $x^n y = C$; $n = 1.60$; $\log C = 0.554$.

Water.		Benzol.		
Calc.	Found.	Calc.	Found.	log C.
19.87	20.00	0.03	0.03	0.557
10.65	10.00	0.09	0.08	0.503
7.94	8.00	0.13	0.13	0.559
4.97	5.00	0.273	0.275	0.557
4.00	4.00	0.39	0.39	0.554
3.02	3.00	0.61	0.61	0.558
2.01	2.00	1.18	1.17	0.550
1.72	1.72	1.50	1.50	0.553
1.50	1.50	1.87	1.87	0.554
1.44	1.45	1.98	2.00	0.559
1.00	1.00	3.58	3.57	0.553
0.605	0.605	8.00	8.00	0.554
0.526	0.525	10.04	10.00	0.552
0.34	0.34	20.14	20.00	0.551
			Average,	0.551

TABLE V.

x c.c. Water; y c.c. Benzol; 5 c.c. Methyl Alcohol. Temp. 20°.

Formula $x^{n_1} y = C_1$; $n_1 = 1.48$; $\log C_1 = 0.216$.

Water.		Benzol.		
Calc.	Found.	Calc.	Found.	log C_1.
5.05	5.00	0.15	0.15	0.211
3.95	4.00	0.21	0.215	0.223
3.01	3.00	0.32	0.32	0.211
2.00	2.00	0.59	0.59	0.216
1.40	1.40	1.00	1.00	0.216
			Average,	0.215

Formula $x^{n_2} y = C_2$; $n_2 = 2.00$; $\log C_2 = 0.281$.

				log C_2.
1.13	1.13	1.50	1.50	0.282
1.00	1.00	1.91	1.90	0.279
0.80	0.80	2.99	3.00	0.283
0.69	0.69	4.01	4.00	0.280
0.49	0.49	7.96	8.00	0.283
			Average,	0.281

TABLE VI.

x c.c. Water; y c.c. Benzol; 5 c.c. Acetone. Temp. 20°.

Formula $x^{n_1} y = C_1$; $n_1 = 1.40$; $\log C_1 = 0.262$.

Water.		Benzol.		
Calc.	Found.	Calc.	Found.	log C_1.
7.97	8.00	0.10	0.10	0.264
7.00	7.00	0.12	0.12	0.262
5.04	5.00	0.19	0.19	0.258
4.03	4.00	0.26	0.26	0.258
2.99	3.00	0.393	0.395	0.264
2.49	2.50	0.51	0.51	0.265
2.18	2.20	0.61	0.615	0.269
2.01	2.00	0.69	0.69	0.260
			Average,	0.2625

Formula $x y^{n_2} = C_2$; $n_2 = 1.35$; $\log C_2 = 0.114$.

				log C_2.
1.67	1.67	0.833	0.833	0.114
1.50	1.50	0.90	0.90	0.114
1.30	1.30	1.00	1.00	0.114
1.005	1.00	1.215	1.21	0.112
0.65	0.65	1.67	1.67	0.114
0.51	0.51	2.00	2.00	0.114
0.38	0.38	2.49	2.50	0.116
0.295	0.295	3.00	3.00	0.114
0.20	0.20	4.00	4.00	0.114
0.15	0.15	4.96	5.00	0.119
			Average,	0.1145

There is but one exception, in the chloroform-water-acetone series. As chloroform and water behave normally with alcohol (Table I.), water and acetone with benzol (Table VI.), the disturbing effect must be due to chloroform and acetone in presence of each other. I have not yet had time to investigate mixtures of chloroform and acetone in the absence of water, to determine whether they are abnormal in respect to any other physical properties. In the other five cases the agreement between observed and calculated values is a remarkable one, well within the limits of experimental error, and this in spite of the wide range that the measurements cover. In the benzol-water-alcohol series the ratio of benzol to water varies as one to forty thousand; in the chloroform-water-alcohol series the ratio chloroform-water varies as one to twelve thousand. In the last measurement of Table I. the chloroform forms over 85% by volume synthetically of the solution, so that in this instance we are well beyond the realms of the "dilute solutions," without noticing any disturbing effect due to "variations from the gas laws." The series benzol-water-alcohol is represented by a single curve; but it must not be thought that in this it forms a real exception to the other mixtures. Theoretically, there are two curves for this series; but the two happen to have the same direction, and therefore appear as one. The point where the precipitate ceases to be less dense than the original solution lies between the mixtures benzol 2.00 c.c., water 1.45 c.c., and benzol 3.57 c.c., water 1.00 c.c.

The formula $x^\alpha y^\beta =$ Constant is not satisfactory, because it contains no term expressing the variation of the consolute liquid in case one of the non-miscible liquids is kept constant, and also because a change in the units in which x and y are expressed or a change in the amount of the consolute liquid taken affects the constant of the formula. This can be remedied by the following reasoning. According to Gibbs and to experiment, the absolute mass of a phase has no effect on the equilibrium. Therefore increasing the quantities of x and y m-fold involves increasing the quantity of the consolute liquid m-fold if the solutions are to remain at the saturation point. This would increase the value of the constant $m^{\alpha+\beta}$ times. If then x and y denote the values in cubic centimeters of the non-miscible liquids A and B, z the corresponding value for the consolute liquid S, we have as equation of equilibrium for saturated solutions the expression:

I.
$$\frac{x^\alpha y^\beta}{z^{\alpha+\beta}} = C.$$

If, as was done, z is kept constant, this simplifies to formula (4), which I will renumber Ia.

Ia.
$$x^\alpha y^\beta = C_1.$$

If y is constant, x and z varying, we have:

Ib.
$$\frac{x^\alpha}{z^{\alpha+\beta}} = C_2.$$

And if x is constant, y and z varying, we have:

Ic.
$$\frac{y^\beta}{z^{\alpha+\beta}} = C_3.$$

In equation I the value of C is a function of the nature of the units in which x, y, and z are expressed; but independent of the size. Thus grams and kilograms give the same result, cubic centimeters and litres; but the weight constant is different from the volume constant, and the constants for reacting weights or reacting volumes would have still other values. C is also dependent on the absolute value of the exponential factors α and β. We can however eliminate this effect by writing

$$C = K^{\alpha+\beta}, \tag{6}$$

in which case K remains entirely unchanged, when we substitute $\frac{\alpha}{\beta} = n$. In Table VII. I give in the first two columns the values for log C according to the general formula $\frac{x^n y}{z^{n+1}} = C$, when x, y, and z are expressed in volumes. Since $z = 5$ in all these measurements, Table VII. gives the constants of the preceding tables less the corresponding values of $(n + 1) \log 5$. It would have been better to calculate the integration constant using the rational exponents α and β; but only their ratio can be determined by a study of equilibrium in one liquid layer, and the case of two liquid layers will form the subject of a separate communication. In columns three and four are the corresponding values of K_1 and K_2 according to equation (6). They are the constants of the preceding two columns divided by the appropriate values of $n + 1$.

TABLE VII.

Mixtures.	log C_1.	log C_2.	log K_1.	log K_2.
H_2O, $CHCl_3$, C_2H_5OH	$\bar{1}.163$	$\bar{1}.266$	$\bar{1}.711$	$\bar{1}.652$
H_2O, $CHCl_3$, CH_3OH	$\bar{2}.984$	$\bar{1}.489$	$\bar{1}.692$	$\bar{1}.773$
H_2O, $CHCl_3$, CH_3COCH_3	$\bar{2}.506$	....	$\bar{1}.381$	....
H_2O, C_6H_6, C_2H_5OH	$\bar{2}.737$	$\bar{2}.737$	$\bar{1}.514$	$\bar{1}.514$
H_2O, C_6H_6, CH_3OH	$\bar{2}.482$	$\bar{2}.184$	$\bar{1}.388$	$\bar{1}.395$
H_2O, C_6H_6, CH_3COCH_3	$\bar{2}.584$	$\bar{2}.471$	$\bar{1}.410$	$\bar{1}.349$

The values given under x and y in Tables I.–VI. are amounts of the liquids A and B in a given quantity of S, — in this case 5 c.c. A glance at the tables will show that these figures are very far from expressing volume concentrations, i. e. quantity of substance in a given volume of the solution. As most theoretical generalizations in chemistry are expressed in volume concentrations, it will be necessary to see what effect such a change would have on general Formula I. If there is no contraction or expansion on mixing, the volume of the solution will be the sum of the component volumes, or $V = x + y + z$, and the volume concentrations will be $\frac{x}{x+y+z}$, $\frac{y}{x+y+z}$, $\frac{z}{x+y+z}$, respectively. This simple case may be said never to occur, and the volume of the solution is an at present unknown function of the component volumes represented by the expression $V = F(x, y, z)$. While the knowledge of the form of this function is necessary to enable us to calculate the volume concentrations of a given solution from our experimental data, it is superfluous in the present discussion. We have (from Formula I.):

$$\alpha \log x + \beta \log y - (\alpha + \beta) \log z = \log C.$$

Now $$\alpha \log V + \beta \log V - (\alpha + \beta) \log V = 0,$$

$$\therefore \quad \alpha \log \frac{x}{V} + \beta \log \frac{y}{V} - (\alpha + \beta) \log \frac{z}{V} = \log C;$$

or $\frac{x^{\alpha}\, y^{\beta}}{z^{\alpha + \beta}} = C$, if x, y, and z denote volume concentrations instead of having their previous significance. Since α, β, and C remain unchanged, we find that Equation I represents the series of saturated solutions obtained at constant temperature with any two non-miscible liquids, and a third liquid miscible in all proportions with each of the other two, provided no chemical reaction takes place and provided the reacting weights of the liquids remain unchanged. It is immaterial whether x, y, and z denote volume concentrations, or concentrations of two of the substances in a constant quantity of the third.

As has been said, volume concentrations are generally looked upon as the only scientific way of expressing data. This is perfectly natural when we remember that our theoretical ideas have been formed almost entirely upon a study of the gaseous state. It is not a necessary method, and in this particular case it is decidedly disadvantageous practically to use volume concentrations. It involves a determination of the density of each solution, increasing the work and bringing in a new source of error. When expressed in volume concentrations all three components vary, and while it is a simple matter to plot three variables in a plane,* I know of no way in which this can be done for the logarithms of these variables. By the method which I have followed, one constituent can be kept constant, no density determinations are necessary, and there are only two variables. The formula being hyperbolic, by plotting the data on logarithmic co-ordinates one gets a straight line, any variation from which is easily seen, while the constants of the curve can be determined from the diagram with more speed and accuracy than by substituting the experimental values in an equation and solving for two unknown quantities.

The next case to be considered is when we have two partially miscible liquids, and a third miscible in all proportions with each of the others. Formula I cannot apply here, because it was deduced for two non-miscible liquids, and this condition is no longer fulfilled. There are two ways of treating a problem like this. One is to change the conditions of the experiment until they agree with the formula. The other is to change the formula till it conforms to the conditions of the experiment. I have done both. I will suppose, for the sake of clearness, that the two partially miscible liquids are ether and water. Saturated solutions of water in ether are absolutely non-miscible at the temperature for which they are saturated, being thus an improvement over benzol and water, which are slightly miscible theoretically. If x and y in equation Ia mean quantities of saturated water and saturated ether solutions, instead of pure water and pure ether, the conditions are satisfied for which this formula was deduced, and the equation must apply. I have found that it did, and the experimental proof is given in Tables IX. and XI.

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* Gibbs, Thermodynamische Studien, p. 141; Roozeboom, Zeitschr. f. ph. Chem., XII. 369, 1893.

This being settled, we can attack the second part of the problem. Let X denote cubic centimeters of saturated solution of ether in water, Y cubic centimeters of saturated solution of water in ether which saturate a given quantity of a consolute liquid. It is found experimentally that

$$X^{\alpha} Y^{\beta} = \text{Constant}, \tag{7}$$

or, if we set $\frac{\alpha}{\beta} = n$, we shall have

$$X^{n} Y = C. \tag{8}$$

If s_1 is the solubility of ether in water, s_2 the solubility of water in ether, both expressed in volumes per cubic centimeter of the solvent synthetically, we shall have, if no contraction or expansion takes place in forming the saturated solutions of water in ether and ether in water:

$$X = A + s_1 A; \quad Y = B + s_2 B; \tag{9}$$

$$(A + s_1 A)^n (B + s_2 B) = C; \tag{10}$$

where A = c.c. water in X, B_2 = c.c. ether in Y. As we must assume some contraction or expansion, let the ratio of the actual volume to the sum of the component volumes be σ_1 in the saturated solution of ether in water, and σ_2 in the saturated solution of water in ether. We have then:

$$X = \sigma_1 (A + s_1 A); \quad Y = \sigma_2 (B + s_2 B); \tag{11}$$

$$\{\sigma_1 (A + s_1 A)\}^n \{\sigma_2 (B + s_2 B)\} = C_1; \tag{12}$$

which can be rewritten:

$$(13)\qquad (A + s_1 A)^n (B + s_2 B) = \frac{C_1}{\sigma_1{}^n \sigma_2}.$$

If x and y denote cubic centimeters of pure water and pure ether dissolved in a given quantity of the consolute liquid, we have:

$$(14)\qquad x = A + s_2 B; \quad y = B + s_1 A.$$

Solving for A and B: —

$$(15)\qquad A = \frac{x - s_2 y}{1 - s_1 s_2}; \quad B = \frac{y - s_1 x}{1 - s_1 s_2}.$$

Substituting these values in (13): —

$$(16)\qquad \left\{ \frac{1 + s_1}{1 - s_1 s_2} (x - s_2 y) \right\}^n \left\{ \frac{1 + s_2}{1 - s_1 s_2} (y - s_1 x) \right\} = \frac{C_1}{\sigma_1{}^n \sigma_2}.$$

Since σ_1, σ_2, s_1, s_2, are constants for constant temperature, we can simplify equation (16) into:

$$(17)\qquad (x - s_2 y)^n (y - s_1 x) = C_2,$$

where the relation between C_1 and C_2 is

$$(18)\qquad \frac{C_1}{C_2} = \frac{\sigma_1{}^n \sigma_2 (1 + s_1)^n (1 + s_2)}{(1 - s_1 s_2)^{n+1}}.$$

Eliminating the effect due to the arbitrary quantity of consolute liquid used, we have:

$$(19)\qquad \frac{(x - s_2 y)^n (y - s_1 x)}{z^{n+1}} = C_3;$$

where $C_3 = \frac{C_2}{z^{n+1}}$. Reverting to the most general form, so as to make the equation correspond in form to Equation I.,

$$\text{II.}\qquad \frac{(x - s_2 y)^\alpha (y - s_1 x)^\beta}{z^{\alpha+\beta}} = C.$$

Equation II. is more general than Equation I., the latter being merely a special case of the former, where the terms representing the mutual solubilities are so small that they can be neglected.

In testing these equations I took, as pairs of partially miscible liquids, ether and water, ethylacetate and water. The ether was distilled over sodium, the ethylacetate dried with calcium chloride and fractionated, the boiling point rising a full degree for a litre distilled off. I think however that no essential error was introduced in this way, and that, for my purposes, it was sufficiently pure. The solubilities were determined volumetrically. In all cases I took 10 c.c. of the solvent in a test tube and ran in the solute from a burette till the solution clouded. One can determine this point to 0.01 c.c. without difficulty. In Table VIII. I give the solubilities at 20° expressed in cubic centimeters of solute in ten cubic centimeters of solvent. The solubilities of ether and ethylacetate in water decrease with increasing temperature; the solubilities of water in ether and ethylacetate increase with increasing temperature. This behavior is well known for ether; but I have not found it stated anywhere for ethylacetate.

TABLE VIII.

Solute	Solvent.	Solubility.
Ether	Water	1.03–4 *
Water	Ether	0.08
Ethylacetate	Water	0.926
Water	Ethylacetate	0.294

It will be remembered that, when two liquids were practically non-miscible, the series of saturated solutions formed by these with a consolute liquid were expressed by two curves of the same general form, but having different constants; and it was found that these two curves represented, the one the series of solutions out of which liquid *B* is precipitated on addition of either *A* or *B*; the other, the converse series, when the solution was saturated in respect to *A* but sensitive to an excess of either *A* or *B*. When the liquids *A* and *B* are partially miscible, the case becomes apparently more complicated, for we have four curves instead of two. These refer to four distinct sets of equilibrium, there being the following four series of saturated solutions.

1. The solution is saturated in respect to *B*. Excess of *A* produces no precipitate.
2. The solution is saturated in respect to *B*. Excess of *A* or *B* produces a precipitate of *B*.
3. The solution is saturated in respect to *A*. Excess of *A* or *B* produces a precipitate of *A*.
4. The solution is saturated in respect to *A*. Excess of *B* produces no precipitate.

Series 2 and 3 correspond to the two series observed with two non-miscible liquids. In these two series the consolute liquid is the solvent, whereas in series 1 and 4 we have, in addition, *A* and *B* respectively as solvents. In Tables IX.–XIII. I give the measurements made with ether and water, ethylacetate and water with the consolute liquids alcohol, methylalcohol, and acetone. In Tables IX. and XI. the experiments were made with saturated solutions; in Tables X., XII., and XIII., with pure liquids. The first method has the advantage that the readings obtained are final, involving no correction and no knowledge of the mutual solubilities. On the other hand, it is necessary to keep the solutions in the burettes at the same temperature as that at which one makes the determinations, a very difficult thing to do usually, so that the second method is to be preferred. The exponential factors are the same according to both methods, as I have already shown. The integration constants are different, standing to each other in the relation given in Equation (18). It would have been well if I had determined the densities of the saturated solutions so that they could be recalculated into cubic centimeters of the pure liquids; but I shall have to make an extended series of density determinations in connection with the equilibrium between two liquid phases, and I have postponed these others till then. The measurements in Tables IX.–XIII. are about as accurate as those in Tables I.–VI., with the exception of the solutions when water is part solvent. The precipitate in these cases is lighter than the solution, consists of a few drops only, and is very difficult to distinguish from air bubbles, especially in the ether solutions, where the clouding at best is very slight. For this reason the first series in each table must be considered as very doubtful as the absolute measurements go. The determination of the saturation point for these cases depended on the light, the state of my eyes, and the mood which I happened to be in on the days when the measurements were made. So difficult are the determinations sometimes, that I give no results for ether-water-acetone because I obtained different measurements every day. The agreement between the observed and the theoretical values is no test of the absolute accuracy of either; but merely shows that the solutions follow the same general law, the constants, exponential, and integration varying with the degree of cloudiness which the observer takes as denoting the point of saturation. The values of n are not so accurate as in the first set of tables, because the curves cover a more limited extent, and therefore the variations are smaller, and because when the value of n is large, say over 2, a very slight change in the direction of the logarithmic curve produces a very large corresponding change in n. The amounts of ethylacetate and water which dissolve in 5 c.c. of alcohol, methylalcohol, or acetone were so large that I was forced to work with one cubic centimeter of these liquids as solvent.

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* Schuncke finds 1.04–5, Zeitschr. f. ph. Chem., XIV. 334. 1894.

TABLE IX.

X c.c. Sat. Water; Y c.c. Sat. Ether; 5 c.c. Alcohol. Temp. 20°.

Formula $X Y^{n_1} = C_1$; $n_1 = 2.60$; log $C_1 = 1.994$.

Sat. Water.		Sat. Ether.		
Calc.	Found.	Calc.	Found.	log C_1.
49.89	50.00	1.30	1.30	1.995
24.89	25.00	1.70	1.70	1.996
10.02	10.00	2.41	2.41	1.993
			Average,	1.995

Formula $X^{n_2} Y = C_2$; $n_2 = 1.49$; log $C_2 = 1.867$.

				log C_2.
9.04	9.00	2.79	2.77	1.864
7.96	8.00	3.33	3.35	1.870
7.72	7.70	3.52	3.50	1.865
6.00	6.00	5.10	5.10	1.867
			Average,	1.867

Formula $X Y = C_3$; log $C_3 = 1.493$.

				log C_3.
5.19	5.21	5.97	6.00	1.495
4.45	4.45	7.00	7.00	1.493
3.99	4.00	7.78	7.80	1.494
3.89	3.87	8.03	8.00	1.491
3.11	3.10	10.05	10.00	1.491
2.08	2.08	14.95	15.00	1.495
1.78	1.77	17.58	17.50	1.491
			Average,	1.493

Formula $X^{n_4} Y = C_4$; $n_4 = 1.73$; log $C_4 = 1.665$.

				log C_4.
1.62	1.61	20.28	20.00	1.661
1.43	1.43	24.95	25.00	1.673
1.09	1.10	39.27	40.00	1.666
0.96	0.95	50.47	50.00	1.659
			Average,	1.665

TABLE X.

x c.c. Water; y c.c. Ether; 1 c.c. Methyl Alcohol. Temp. 20°.

Formula $(x - 0.008\,y)\,(y - 0.103\,x)^{n_1} = C_1$; $n_1 = 1.50$; log $C_1 = \bar{1}.502$.

Water.		Ether.		
Calc.	Found.	Calc.	Found.	log C_1.
10.05	10.00	1.13	1.13	$\bar{1}.500$
9.00	9.00	1.04	1.04	$\bar{1}.502$
7.03	7.00	0.85	0.85	$\bar{1}.500$
4.97	5.00	0.68	0.68	$\bar{1}.505$
4.00	4.00	0.60	0.60	$\bar{1}.502$
				$\bar{1}.502$

Formula $(x - 0.008\,y)^{n_2}\,(y - 0.103\,x) = C_2$; $n_2 = 1.13$; $\log C_2 = \bar{1}.928$.

Water.		Ether.		
Calc.	Found.	Calc.	Found	log C_2.
2.95	3.00	0.555	0.56	$\bar{1}.936$
2.50	2.50	0.56	0.56	$\bar{1}.928$
2.03	2.00	0.60	0.59	$\bar{1}.920$
1.80	1.80	0.63	0.63	$\bar{1}.929$
1.50	1.50	0.70	0.70	$\bar{1}.929$
				$\bar{1}.928$

Formula $(x - 0.008\,y)^{n_3}\,(y - 0.103\,x) = C_3$; $n_3 = 2.04$; $\log C_3 = 0.045$.

				log C_3.
1.20	1.20	0.90	0.90	0.047
1.00	1.00	1.23	1.23	0.045
0.90	0.89	1.53	1.50	0.035
0.83	0.83	1.79	1.80	0.047
0.78	0.78	2.00	2.00	0.046
0.64	0.64	3.01	3.00	0.043
0.57	0.57	3.99	4.00	0.047
0.52	0.52	5.00	5.00	0.045
0.47	0.47	6.89	7.00	0.053
				0.045

Formula $(x - 0.008\,y)^{n_4}\,(y - 0.103\,x) = C_4$; $n_4 = 4.4$; $\log C_4 = \bar{1}.057$.

				log C_4.
0.44	0.44	10.30	10.00	$\bar{1}.044$
0.45	0.45	11.62	12.00	$\bar{1}.071$
0.45	0.45	15.04	15.00	$\bar{1}.056$
				$\bar{1}.057$

TABLE XI.

X c.c. Sat. Water; Y c.c. Sat. Ethylacetate; 1 c.c. Alcohol. Temp. 20°.

Formula $X\,Y^{n_1} = C_1$; $n_1 = 2.86$; $\log C_1 = \bar{1}.280$.

Sat. Water.		Sat. Ethylacetate.		
Calc.	Found.	Calc.	Found.	log C_1.
10.05	10.00	0.25	0.25	$\bar{1}.278$
8.07	8.00	0.27	0.27	$\bar{1}.276$
7.11	7.00	0.28	0.28	$\bar{1}.263$
5.97	6.00	0.30	0.30	$\bar{1}.282$
4.97	5.00	0.32	0.32	1.283
3.94	4.00	0.34	0.35–	$\bar{1}.286$
			Average,	$\bar{1}.278$

Formula $X^{n_2} Y = C_2$; $n_2 = 1.80$; $\log C_2 = 0.549$.

Sat. Water.		Sat. Ethylacetate.		
Calc.	Found.	Calc.	Found.	log C_2.
3.00	3.00	0.49	0.49	0.549
2.50	2.50	0.68	0.68	0.548
2.00	2.00	1.02	1.02	0.550
			Average,	0.549

Formula $X^{n_3} Y = C_3$; $n_3 = 1.36$; $\log C_3 = 0.433$.

				log C_3
1.45	1.50	1.56	1.59	0.445
1.25	1.25	2.00	2.00	0.433
1.06	1.06	2.51	2.50	0.432
1.00	1.00	2.71	2.72	0.434
0.93	0.92	3.04	3.00	0.428
0.75	0.75	4.00	4.00	0.432
			Average,	0.434

Formula $X^{n_4} Y = C_4$; $n_4 = 1.765$; $\log C_4 = 0.372$.

				log C_4.
0.65	0.65	5.02	5.00	0.369
0.59	0.59	5.98	6.00	0.373
0.54	0.54	7.00	7.00	0.372
0.50	0.50	8.00	8.00	0.372
0.44	0.44	9.96	10.00	0.370
			Average,	0.371

TABLE XII.

x c.c. Water; y c.c. Ethylacetate; 1 c.c. Methyl Alcohol. Temp. 20°.

Formula $(x - 0.029\,y)\,(y - 0.093\,x)^{n_1} = C_1$; $n_1 = 1.20$; $\log C_1 = 0.002$.

Water.		Ethylacetate.		
Calc.	Found.	Calc.	Found.	log C_1.
9.92	10.00	1.08	1.08	0.006
6.96	7.00	0.85	0.85	0.005
5.08	5.00	0.72	0.72	$\bar{1}.995$
3.96	4.00	0.69	0.69	0.006
3.01	3.00	0.68	0.68	0.000
2.51	2.50	0.70	0.70	0.001
			Average,	0.002

Formula $(x - 0.029\,y)^{n_2}\,(y - 0.093\,x) = C_2$; $n_2 = 2.78$; $\log C_2 = 0.631$.

				log. C_2.
2.03	2.00	0.83	0.82	0.637
1.80	1.80	1.04	1.04	0.630
1.72	1.70	1.19	1.15	0.617
1.49	1.50	1.63	1.69	0.644
1.41	1.41	1.99	2.00	0.633
			Average,	0.632

Formula $(x - 0.029\,y)^{n_3}\,(y - 0.093\,x) = C_3$; $n_3 = 2.00$; $\log C_3 = 0.550$.

Water.		Ethylacetate.		
Calc.	Found.	Calc.	Found.	log. C_3.
1.29	1.29	2.51	2.50	0.549
1.20	1.20	2.99	3.00	0.551
1.07	1.07	4.03	4.00	0.547
1.00	1.00	4.88	4.90	0.552
			Average,	0.550

Formula $(x - 0.029\,y)^{n_4}\,(y - 0.093\,x) = C_4$; $n_4 = 7.00$; $\log C_4 = 0.078$.

				log C_4.
0.97	0.97	6.00	6.00	0.078
0.98	0.98	7.02	7.00	0.076
1.00	1.00	7.61	8.00	0.100
1.03	1.03	9.98	10.00	0.079
			Average,	0.083

TABLE XIII.

x c.c. Water ; y c.c. Ethylacetate ; 1 c.c. Acetone. Temp. 20°.

Formula $(x - 0.029\,y)\,(y - 0.093\,x)^{n_1} = C_1$; $n_1 = 1.54$; $\log C_1 = \bar{1}.364$.

Water.		Ethylacetate.		
Calc.	Found.	Calc.	Found.	log C_1.
10.12	10.00	1.02	1.01	$\bar{1}.359$
6.99	7.00	0.76	0.76	$\bar{1}.365$
5.01	5.00	0.60	0.60	$\bar{1}.363$
3.00	3.00	0.47	0.47	$\bar{1}.364$
2.00	2.00	0.43	0.43	$\bar{1}.365$
			Average,	$\bar{1}.363$

Formula $(x - 0.029\,y)^{n_2}\,(y - 0.093\,x) = C_2$; $n_3 = 1.16$; $\log C_2 = \bar{1}.721$.

				log C_2.
1.50	1.50	0.47	0.47	$\bar{1}.721$
1.00	1.00	0.63	0.63	$\bar{1}.721$
			Average,	$\bar{1}.721$

Formula $(x - 0.029\,y)\,(y - 0.093\,x)^{n_3} = C_3$; $n_3 = 1.26$; $\log C_3 = \bar{1}.653$.

				log C_3
0.79	0.80	0.74	0.74	$\bar{1}.656$
0.69	0.69	0.80	0.80	$\bar{1}.652$
0.51	0.51	1.00	1.00	$\bar{1}.652$
0.31	0.31	1.50	1.50	$\bar{1}.653$
			Average,	$\bar{1}.653$

Formula $(x - 0.029\,y)^{n_4}\,(y - 0.093\,x) = C_4$; $n_4 = 3.00$; $\log C_4 = \bar{2}.135$.

Water.		Ethylacetate.		
Calc.	Found.	Calc	Found.	log C_4.
0.25	0.25	2.01	2.00	$\bar{2}.134$
0.25–	0.25	2.48	2.50	$\bar{2}.138$
0.286	0.285	3.01	3.00	$\bar{2}.134$
0.29	0.29	5.00	5.00	$\bar{2}.135$
			Average,	$\bar{2}.135$

In this set of tables, as in the first set, the amount of one non-miscible liquid which will dissolve in the consolute liquid decreases as the quantity of the other non-miscible liquid increases. In this case, however, the non-miscible liquids are saturated solutions and it does not follow that the quantity of one pure liquid decreases as the other increases. There comes a point where the rate of increase of one component in the solution in which it is solute is greater than its rate of decrease in the solution in which it is solvent. If we take the general Equation (17),

$$(x - s_2\,y)^n\,(y - s_1\,x) = C_2,$$

it is obvious that as x increases y will first decrease, pass through a minimum, and then increase. If the same equation expressed the two equilibria, the point where y was a minimum would be the point where the solution is no longer sensitive to an excess of x. In general, the equilibrium for this second stage is given by a second equation, and all we can say in our present knowledge is that at the intersection of these two curves y should have a minimum value. This does not seem to hold in Table XII., where the amount of ethylacetate soluble in 1 c.c. methylalcohol in presence of 2.50 c.c. water is more than will dissolve when either three or four cubic centimeters of water are added. I am inclined to attribute this to experimental error, as I do not see how there can be two saturated solutions of the same substance in the same solvent. Such a case would be entirely new, and would involve such consequences that it is not to be assumed on the strength of a variation of two one-hundredths of a cubic centimeter on measurements where the probable error is known to be very large. I propose to repeat these measurements on a larger scale, so as to determine what the facts really are. There are also one or two things in respect to the ether-water-methylalcohol curve which need to be gone into more closely. In Table XIV. I give the values for log C when cleared of the term for z, and the values for log K when the effect of the exponential factor has been eliminated. Both log C and log K are calculated for x, y, and z being expressed in cubic centimeters. A discussion of these values is not possible at present, and in any case they should be reduced to reacting volumes or eacting weights before a rational treatment could be thought of.

TABLE XIV.

Mixtures.	log C_1.	log C_2.	log C_3.	log C_4.	log K_1.	log K_2.	log K_3.	log K_4.
S. H_2O, S. Ether, Alcohol	$\bar{1}.478$	0.126	0.095	$\bar{1}.757$	$\bar{1}.855$	0.051	0.047	$\bar{1}.911$
H_2O, Ether, Methylalcohol	$\bar{1}.502$	$\bar{1}.928$	0.045	$\bar{1}.057$	$\bar{1}.801$	$\bar{1}.966$	0.015	$\bar{1}.825$
S. H_2O, S. Et. Ac., Alcohol	$\bar{1}.280$	0.549	0.433	0.372	$\bar{1}.814$	0.196	0.182	0.134
H_2O, Et. Ac., CH_3OH	0.002	0.631	0.550	0.078	0.001	0.167	0.183	0.001
H_2O, Et. Ac., Acetone	$\bar{1}.364$	$\bar{1}.721$	$\bar{1}.653$	$\bar{2}.135$	$\bar{1}.749$	$\bar{1}.871$	$\bar{1}.894$	$\bar{1}.534$

The measurements already communicated would be sufficent by themselves to establish the general law governing this class of equilibria; but I have in addition experiments by other investigators which give the same result. In 1871 Tuchschmidt and Follenius* noticed that carbon bisulphide was not infinitely miscible with aqueous alcohol and they made a series of experiments to determine the saturation points when carbon bisulphide was added to alcohol of known strengths. They expressed their results by means of a complex empirical formula. This is not necessary, as the general equation for two non-miscible liquids covers the case entirely. In Table XV. the first column gives the number of cubic centimeters of carbon bisulphide which will dissolve in ten cubic centimeters of aqueous alcohol of the percentage composition by weight given in column two. In column three is the strength of alcohol as required by the formula.

TABLE XV.

x = g. H_2O; y = c.c. CS_2. Temp. 17°.

Formula $x y^n = C$; $n = \frac{8}{5}$; log $C = 1.345$.

	% Alcohol.		
y.	Calc.	Found.	log C.
18.20	9.88	9.85	1.457
13.20	9.80	9.815	1.318
10.00	9.70	9.695	1.345
7.00	9.50	9.354	1.456
5.00	9.15	9.137	1.350
3.00	8.43	8.412	1.324
2.00	7.40	7.602	1.310
0.20	....	4.84	....
		Average,	1.366

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* B. B., IV. 583. 1871.

When one considers that the carbon bisulphide was evidently determined very roughly, the agreement is an excellent one. Here, too, we find the existence of two curves. The last measurement lies on the second curve when water is the precipitate, and not carbon bisulphide. As only one point on this curve was measured, it is impossible to determine the constants even approximately. The object of this investigation by Tuchschmidt and Follenius was to obtain a method for determining the strength of aqueous alcohol quickly and easily. Owing to the unpleasant properties of carbon bisulphide, their choice of liquids was bad, though the method seems to me a good one. If one were to make a complete table for benzol or chloroform and aqueous alcohol at zero degrees, the rest would be simplicity itself. One would take ten cubic centimeters of the alcohol to be tested and run in chloroform from a burette till saturated, when a glance at the table would give the percentage composition of the alcohol. The method would be quicker than any except with a hydrometer, and more accurate than that. An idea of the accuracy is given by the fact that at 20°, 5 c.c. of 96% alcohol require about 20 c.c. chloroform, while the same amount of 97.5% alcohol requires about 30 c.c. for saturation. For a weaker alcohol the change for each per cent is much less ; but the measurements can be made more accurately.

I will now take up the measurements of Pfeiffer * on the miscibility of various esters with alcohol and water. The measurements were not made under the most favorable circumstances. A known amount of the ester was poured into a beaker, a definite quantity of alcohol added, and water run in till the saturation point was reached. Nothing was done to prevent evaporation, nothing, so far as is mentioned, to keep a constant temperature, and there was no means of warming the solution above the final temperature in order to insure that equilibrium had been reached. The necessity of this last had already been pointed out by Duclaux,† who found that, on cooling a solution below its saturation point, it clouded at once ; but on warming, the equilibrium was reached much more slowly. Given these untoward conditions, the comparative accuracy of the measurements is remarkable. While Pfeiffer has given us series upon series of valuable measurements, showing the increase of miscibility of esters and water in presence of alcohol, he has curiously enough omitted all determinations of the miscibility of water and esters when no alcohol is present. This is still

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* Zeitschr. f. ph. Chem., IX. 469. 1892.

† Ann. chim. phys., [5.], VII. 264. 1876.

more remarkable if one considers the uselessness of comparing the effect of equal quantities of alcohol on ethylacetate and water, amylacetate and water, without allowing for the fact that ethylacetate is roughly forty times as soluble in water as amylacetate. As these solubilities had to be known at any rate approximately, in order to apply Equation II. to Pfeiffer's experimental data, I have determined several myself. Through the courtesy of Mr. Dunlap of the organic laboratory, I received small quantities of ethylbutyrate, ethylisovalerate, and isoamylacetate. I dried them over calcium chloride and fractionated. The change of boiling point of the portions used was four degrees for the ethylisovalerate and two degrees for each of the others. The amounts at my disposal made it not worth while to attempt further purification. In Table XVI. I give the solubilities in cubic centimeters of the solute in ten cubic centimeters of the solvent at 20°. For purposes of comparison I have also inserted in this table the values for ethylacetate from Table VIII.

TABLE XVI.

Solute.	Solvent.	Solubility.
Ethylacetate	Water	0.926
Water	Ethylacetate	0.294
Isoamylacetate	Water	0.02
Water	Isoamylacetate	0.12
Ethylbutyrate	Water	0.08
Water	Ethylbutyrate	0.04–5
Ethylisovalerate	Water	0.02–
Water	Ethylisovalerate	0.04+

For these four esters I have found that the solubility in water decreases with increasing temperature, while the solubility of water in the ester increases with increasing temperature, both observations being made at 20°. As there is no obvious reason why these four esters should all be abnormal, it is more than likely that this behavior is characteristic of all esters at ordinary temperatures. As it is improbable that the solubility of the esters in water can continue to decrease indefinitely with increasing temperature, there must be some point where it reaches a minimum, and it is quite possible that a determination of this temperature for different esters might give interesting results. The experiments could be made with great ease as the amount of saponification during the time necessary for a measurement would be very small.

Quite recently, de Hemptinne[*] has determined the solubilities of several esters in water at 25°. His measurements are given in grams of the solute per litre of solution. I have reduced his measurements to cubic centimeters of solute in ten cubic centimeters of solvent by dividing by the densities as far as I could get them out of Landolt and Börnstein's tables and Roscoe and Schorlemmer's text-book, disregarding the difference between a litre of solution and a litre of solvent. The results which I give in Table XVII. are only rough approximations, but quite sufficient for my purpose. The figures in the second column are the densities used in recalculating de Hemptinne's figures.

XVII.

Solute.	Solubility	Density.
Isobutylacetate	0.07	0.88
Amylacetate	0.02–	0.88
Methylbutyrate	0.115	0.94
Ethylbutyrate	0.08–	0.898
Amylbutyrate	0.006	0.85
Propylpropionate	0.06+	0.88
Amylpropionate	0.01+	0.88
Ethylvalerate	0.03	0.86

De Hemptinne did not measure the solubility of water in the esters, and I have not been able to find any data on the subject beyond the few measurements which I have made myself. In considering Pfeiffer's results, this is not very serious, because he worked always with three cubic centimeters of esters, adding alcohol in varying quantities, and water to saturation. As the solubility of water in the different esters can be rarely more than one per cent, the error in calculating the amount of water required to saturate will in no case be more than a tenth of a cubic centimeter, and will rarely exceed two or three hundredths. The solubilities of esters in water, which have not been determined by de Hemptinne or myself, have been filled in as best I could by analogy, remembering that increase of carbon means decrease of solubility, and that among isomeric esters the one with the smaller acid radical was rather the less soluble. In deciding where between two limits an unknown solubility should be put, I have taken the figure which satisfied the experimental data best. The solubilities thus obtained lay no claim to being accurate; but they are not very far out, probably in no case more than 100%, and this rough approximation is better than treating the esters and water as absolutely non-miscible. In Table XVIII. I give the solubilities which I have used in calculating Pfeiffer's results, expressed in cubic centimeters of the ester in ten cubic centimeters of water.

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[*] Zeitschr. f. ph. Chem., XIII. 561. 1894.

XVIII.

Solute.	Solubility.	Solute.	Solubility.
Methylvalerate	0.20	Propylacetate	0.30
Ethylvalerate	0.03	Butylacetate	0.07
Methylbutyrate	0.12	Amylacetate	0.02
Ethylbutyrate	0.08	Propylformiate	0.40
Propylbutyrate	0.02	Butylformiate	0.10
Ethylpropionate	0.30	Amylformiate	0.05
Propylpropionate	0.065		

Starting, as Pfeiffer did, with a constant quantity of ester, his results necessarily lie almost entirely along the curve representing the equilibrium when addition of water or ester produces a precipitate of ester. In a few cases there are a few measurements, never more than two, on the curve where water or ester produces a precipitate of water. There are not enough of these measurements to enable me to determine the direction of this second curve, and in the tables I have therefore given no calculated values in these cases. The point where, according to Pfeiffer, infinite miscibility occurs is the beginning of the curve where the solution is saturated in regard to ester; but water produces no precipitate. The corresponding curve where the solution is saturated in respect to water, while addition of ester produces no precipitate, did not come within the scope of Pfeiffer's investigations at all. It will be noticed that in the last measurements of each series the amount of water required to saturate is very generally greater than the theoretical quantity. I attribute this variation entirely to experimental error. When one is working with one hundred cubic centimeters of solution or more, it becomes almost impossible to determine the first appearance of clouding with great accuracy. In Tables XIX. to XXXI. I give Pfeiffer's results, with the values for the water calculated according to the formula at the top of each table. It is only fair to Herr Pfeiffer to say that, if I had arranged the exponential factors so that z should have been raised to the first power only, the differences between the observed and the calculated values would have been less than they now are. I felt, however, that, as the water was the thing I was calculating, I would make its exponential factor unity instead of that of the alcohol.

TABLE XIX.

y = 3 c.c. Methylvalerate ; x = c.c. Water ; z = c.c. Alcohol.

Formula $x\,(y - 0.02\,x)^{0.37} / z^{1.37} = C$; $\log C = \bar{1}.807$.

	x.		
z.	Calc.	Found.	log C.
3	....	1.66	....
6	5.04	5.06	$\bar{1}.809$
9	8.88	9.03	$\bar{1}.815$
12	13.28	13.40	$\bar{1}.809$
15	18.34	18.41	$\bar{1}.809$
18	23.90	24.00	$\bar{1}.809$
21	30.09	30.09	$\bar{1}.807$
24	36.80	36.72	$\bar{1}.806$
27	44.35	44.15	$\bar{1}.805$
30	52.80	52.37	$\bar{1}.803$
33	62.60	62.25	$\bar{1}.804$
36	74.25	74.15	$\bar{1}.806$
39	91.45	91.45	$\bar{1}.807$
42	....	∞	$\bar{1}.807$

TABLE XX.

y = 3 c.c. Ethylvalerate ; x = c.c. Water ; z = c.c. Alcohol.

Formula $x\,(y - 0.003)^{0.40} / z^{1.40} = C$; $\log C = \bar{1}.682$.

	x.		
z.	Calc.	Found.	log C.
3	....	1.42	....
6	3.81	4.14	$\bar{1}.718$
9	6.73	7.18	$\bar{1}.710$
12	10.07	10.51	$\bar{1}.701$
15	13.81	14.13	$\bar{1}.692$
18	17.80	18.09	$\bar{1}.688$
21	22.15	22.40	$\bar{1}.687$
24	26.80	26.83	$\bar{1}.683$
27	31.65	31.70	$\bar{1}.683$
30	36.70	36.62	$\bar{1}.681$
33	42.15	41.81	$\bar{1}.678$
36	47.65	48.00	$\bar{1}.685$
39	53.40	53.13	$\bar{1}.679$
42	59.40	58.35	$\bar{1}.674$
45	65.55	63.60	$\bar{1}.668$
48	71.90	69.97	$\bar{1}.670$
51	78.50	76.90	$\bar{1}.672$
54	83.25	84.25	$\bar{1}.688$
57	92.40	90.53	$\bar{1}.673$
60	99.50	98.60	$\bar{1}.678$

	x.		
z.	Calc.	Found.	log C.
63	106.80	105.20	$\bar{1}.675$
66	114.70	112.80	$\bar{1}.674$
69	122.40	121.90	$\bar{1}.680$
72	130.40	131.00	$\bar{1}.684$
75	138.90	140.20	$\bar{1}.687$
78	148.00	158.70	$\bar{1}.712$
81	157.50	180.00	$\bar{1}.740$
			$\bar{1}.687$

TABLE XXI.

$y = 3$ c.c. Methylbutyrate ; $x =$ c.c. Water ; $z =$ c.c. Alcohol.

Formula $x\,(y - 0.012)^{0.52} \,/\, z^{1.52} = C$; $\log C = \bar{1}.888$.

	x.		
z.	Calc.	Found.	log C.
3	2.33	2.34	$\bar{1}.889$
6	6.75	6.96	$\bar{1}.902$
9	12.67	12.62	$\bar{1}.886$
12	19.90	19.45	$\bar{1}.878$
15	28.38	28.13	$\bar{1}.884$
18	38.76	38.80	$\bar{1}.889$
21	50.85	55.64	$\bar{1}.927$
24	....	∞	$\bar{1}.892$

TABLE XXII.

$y = 3$ c.c Ethylbutyrate ; $x =$ c.c Water ; $z =$ c.c. Alcohol.

Formula $(x - 0.005\,y)\,(y - 0.008\,x)^{0.41} \,/\, z^{1.41} = C$; $\log C = \bar{1}.785$.

	x.		
z.	Calc.	Found.	log C.
3	....	1.66	....
6	4.90	5.00	$\bar{1}.794$
9	8.73	8.81	$\bar{1}.789$
12	13.08	13.10	$\bar{1}.786$
15	17.95	17.82	$\bar{1}.782$
18	23.50	23.25	$\bar{1}.780$
21	29.24	29.04	$\bar{1}.782$
24	35.55	35.16	$\bar{1}.784$
27	42.35	41.75	$\bar{1}.779$
30	49.40	49.05	$\bar{1}.782$
33	57.12	57.00	$\bar{1}.784$
36	65.69	65.73	$\bar{1}.786$
39	75.25	76.02	$\bar{1}.790$
42	84.05	86.58	$\bar{1}.798$
45	94.50	100.57	$(\bar{1}.812)$
48	106.00	115.40	$(\bar{1}.822)$
51	119.50	137.40	$(\bar{1}.846)$
54	....	∞	$\bar{1}.786$

TABLE XXIII.

y = 3 c.c. Propylbutyrate; x = c.c. Water; z = c.c. Alcohol.

Formula $x\,(y - 0.002\,x)^{0.378} / z^{1.378} = C$; $\log C = \bar{1}.651$.

z.	x.		log C.
	Calc.	Found.	
3	....	1.19	....
6	3.49	3.55	$\bar{1}.658$
9	6.11	6.13	$\bar{1}.652$
12	9.05	9.05	$\bar{1}.651$
15	12.31	12.31	$\bar{1}.651$
18	15.92	15.90	$\bar{1}.650$
21	19.63	19.68	$\bar{1}.651$
24	23.72	23.72	$\bar{1}.651$
27	27.92	27.84	$\bar{1}.650$
30	32.20	32.10	$\bar{1}.649$
33	36.71	36.71	$\bar{1}.651$
36	41.66	41.55	$\bar{1}.650$
39	46.64	46.49	$\bar{1}.649$
42	51.56	51.60	$\bar{1}.652$
45	56.80	56.90	$\bar{1}.652$
48	62.64	62.40	$\bar{1}.649$
51	67.84	68.00	$\bar{1}.652$
54	73.93	73.85	$\bar{1}.650$
			$\bar{1}.651$

TABLE XXIV.

y = 3 c.c. Ethylpropionate; x = c.c. Water; z = c.c. Alcohol.

Formula $x\,(y - 0.03\,x)^{0.39} / z^{1.39} = C$; log. $C = \bar{1}.931$.

z.	Calc.	Found.	log C.
3	2.36	2.32	$\bar{1}.924$
6	6.89	6.87	$\bar{1}.930$
9	12.38	12.35	$\bar{1}.930$
12	19.10	19.17	$\bar{1}.933$
15	27.12	27.12	$\bar{1}.931$
18	36.84	36.84	$\bar{1}.931$
21	50.35	50.42	$\bar{1}.932$
24	....	∞	$\bar{1}.930$

TABLE XXV.

$y = 3$ c.c. Propylpropionate; $x =$ c.c. Water; $z =$ c c. Alcohol.

Formula $x\,(y - 0.0065\,x)^{0.45} / z^{1.45} = C$; $\log C = \bar{1}.733$.

	x.		
z.	Calc.	Found.	log C.
3	....	1.58	....
6	4.45	4.70	$\bar{1}.757$
9	8.27	8.35	$\bar{1}.738$
12	12.25	12.54	$\bar{1}.743$
15	17.04	17.15	$\bar{1}.736$
18	22.27	22.27	$\bar{1}.733$
21	28.00	27.83	$\bar{1}.731$
24	34.20	33.75	$\bar{1}.727$
27	40.80	40.24	$\bar{1}.727$
30	47.95	47.15	$\bar{1}.725$
33	55.70	54.65	$\bar{1}.725$
36	63.50	63.18	$\bar{1}.731$
39	72.25	71.59	$\bar{1}.729$
42	81.15	83.05	$\bar{1}.743$
45	91.30	93.91	$\bar{1}.746$
48	102.00	107.46	$\bar{1}.756$
			$\bar{1}.737$

TABLE XXVI.

$y = 3$ c.c. Propylacetate; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x\,(y - 0.03\,x)^{0.23} / z^{1.23} = C$; $\log C = 0.166$.

	x.		
z.	Calc.	Found.	log C.
3	4.44	4.50	0.170
6	10.57	10.48	0.163
9	17.75	17.80	0.167
12	25.95	26.00	0.167
15	35.72	35.63	0.165
18	46.50	47.50	0.178
21	59.00	58.71	0.164
24	....	∞	0.168

TABLE XXVII.

$y = 3$ c.c. Butylacetate; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x\,(y - 0.007\,x)^{0.3} / z^{1.3} = C$; $\log C = \bar{1}.912$.

	x.		
z.	Calc.	Found.	log C.
3	....	2.08	....
6	6.06	6.08	$\bar{1}.914$
9	10.29	10.46	$\bar{1}.920$
12	15.04	15.37	$\bar{1}.922$
15	20.10	20.42	$\bar{1}.918$
18	25.64	25.60	$\bar{1}.911$
21	31.49	31.49	$\bar{1}.912$
24	37.60	37.48	$\bar{1}.911$
27	44.05	43.75	$\bar{1}.909$
30	50.74	50.74	$\bar{1}.912$
33	58.00	59.97	$\bar{1}.927$
			$\bar{1}.916$

TABLE XXVIII.

$y = 3$ c.c. Amylacetate; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x\,(y - 0.02\,x)^{0.294} / z^{1.294} = C$; $\log C = \bar{1}.861$.

	x.		
z.	Calc.	Found.	log C
3	....	1.76	....
6	....	4.24	....
9	9.03	9.03	$\bar{1}.861$
12	13.11	13.24	$\bar{1}.866$
15	17.43	17.52	$\bar{1}.864$
18	22.22	22.22	$\bar{1}.861$
21	26.99	26.99	$\bar{1}.861$
24	32.24	32.14	$\bar{1}.860$
27	37.59	37.23	$\bar{1}.856$
30	42.78	42.66	$\bar{1}.859$
33	48.41	48.41	$\bar{1}.861$
			$\bar{1}.861$

TABLE XXIX.

$y = 3$ c.c. Propylformiate; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x\,(y - 0.04\,x)^{0.38} / z^{1.38} = C$; $\log C = \bar{1}.967$.

z.	x.		$\log C$.
	Calc.	Found.	
3	2.82	2.83	$\bar{1}.969$
6	7.52	7.50	$\bar{1}.966$
9	13.65	13.50	$\bar{1}.962$
12	21.30	21.60	$\bar{1}.973$
15	30.95	30.60	$\bar{1}.962$
18	52.40	53.00	$\bar{1}.972$
21	....	∞	$\bar{1}.967$

TABLE XXX.

$y = 3$ c.c. Butylformiate; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x\,(y - 0.01\,x)^{\frac{1}{3}} / z^{\frac{4}{3}} = C$; $\log C = 0.057$.

z.	Calc.	Found.	$\log C$.
3	3.43	3.45	0.060
6	8.71	8.83	0.063
9	15.02	14.75	0.049
12	22.32	21.45	0.041
15	30.25	29.65	0.048
18	39.00	39.00	0.057
21	48.80	51.80	0.083
24	....	∞	0.057

TABLE XXXI.

$y = 3$ c.c. Amylformiate; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x\,(y - 0.005\,x)^{0.35} / z^{1.35} = C$; $\log C = \bar{1}.808$.

z.	x.		$\log C$.
	Calc.	Found.	
3	....	1.80	....
6	4.92	5.17	$\bar{1}.829$
9	8.54	8.77	$\bar{1}.820$
12	12.63	12.64	$\bar{1}.809$
15	17.10	17.01	$\bar{1}.806$
18	21.90	21.86	$\bar{1}.807$
21	27.06	27.06	$\bar{1}.808$
24	32.50	32.31	$\bar{1}.805$
27	38.31	38.31	$\bar{1}.808$

	x.		
z.	Calc.	Found.	log C.
30	44.40	44.50	$\bar{1}.809$
33	50.71	50.71	$\bar{1}.808$
36	57.20	57.82	$\bar{1}.813$
39	62.70	65.21	($\bar{1}.830$)
42	71.35	77.05	($\bar{1}.842$)
45	78.75	85.10	($\bar{1}.842$)
48	86.55	94.20	($\bar{1}.845$)
			$\bar{1}.811$

In addition to these tables, Pfeiffer made a few measurements on amylalcohol, monochlor-, dichlor , and trichloracetic ester in the presence of alcohol and water. The solubility of amylalcohol in water is given by Roscoe and Schorlemmer as two parts in a hundred, and I have used this value. I could find no data whatsoever in regard to the chloracetic esters, so I have calculated the values on the false assumption that they are non-miscible with water. The effect of this error is seen very markedly in the case of the monochloraceticester, which is undoubtedly the most soluble of the three. I give these tables in spite of the known inaccuracy, because the absolute values of the constants are, for the time being, of little value, whereas it is essential to show that the same general law covers all substances and that the substitution of chlorine for hydrogen does not affect the action of the Mass Law. The coincidence of the three choraceticesters having the same exponential factor is probably only superficial, as the correction for the solubilities would alter the exponential factor somewhat.

TABLE XXXII.

$y = 3$ c.c. Amylalcohol; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x\,(y = 0.02\,x)^{0.4} / z^{1.4} = C$; log $C = 0.100$. Temp. 9.1°.

	x.		
z.	Calc.	Found.	log. C.
3	3.81	3.21	. . . .
6	10.26	10.35	0.104
9	18.53	18.34	0.095
12	28.45	27.47	0.085
15	40.85	41.25	0.104
			0.097

TABLE XXXIII.

$y = 3$ c.c. Amylalcohol; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x\,(y - 0.02\,x)^{0.4} / z^{1.4} = C$; $\log C = 0.112$. Temp. 19.2°.

	x.		
z.	Calc.	Found.	log C
3	3.93	3.50	. . . .
6	10.55	10.80	0.122
9	19.10	19.10	0.112
12	30.05	29.15	0.099
15	42.30	43.15	0.121
			0.114

TABLE XXXIV.

$y = 3$ c.c. Monochloraceticester; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x\,y^{0.43} / z^{1.43} = C$, $\log C = \bar{1}.700$.

	x.		
z.	Calc.	Found.	log C.
3	1.54	1.32	$\bar{1}.644$
6	4.05	4.01	$\bar{1}.695$
9	7.23	7.30	$\bar{1}.705$
12	10.91	10.78	$\bar{1}.695$
15	15.04	16.16	$\bar{1}.731$
18	19.50	22.16	$\bar{1}.756$
21	24.33	28.74	$\bar{1}.772$
			$\bar{1}.714$

TABLE XXXV.

$y = 3$ c.c. Dichloraceticester; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x\,y^{0.43} / z^{1.43} = C$; $\log C = \bar{1}.479$.

	x.		
z.	Calc.	Found.	log C.
3	0.90	0.90	$\bar{1}.477$
6	2.44	2.45	$\bar{1}.481$
9	4.35	4.33	$\bar{1}.477$
12	6.54	6.60	$\bar{1}.482$
15	9.04	9.20	$\bar{1}.487$
			$\bar{1}.481$

TABLE XXXVI.

y = 3 c.c. Trichloraceticester; x = c.c. Water; z = c c. Alcohol.

Formula $x\,y^{0.43} / z^{1.43} = C$; $\log C = \bar{1}.336$.

	x.		
z.	Calc.	Found.	log C.
3	0.65	0.65	$\bar{1}.336$
6	1.76	1.80	$\bar{1}.347$
9	3.13	3.02	$\bar{1}.321$
12	4.72	4.50	$\bar{1}.315$
15	6.50	6.50	$\bar{1}.336$
			$\bar{1}.331$

Tables XIX.–XXXI. furnish a striking confirmation of the way in which the Mass Law applies to this class of phenomena; while some of the results are not as satisfactory, perhaps, as I should like, there are some, notably those with propylbutyrate, where the agreement between the observed and the calculated values is something marvellous, though it is unfortunate that the solubility of propylbutyrate in water has never been determined experimentally.

As it might be thought a mere assumption that the first measurements in several series were determinations of another equilibrium, namely, of a saturated solution from which water or ester precipitated water, I have made a few measurements with the few esters I had on hand. The object of these measurements was to show that the change from one equilibrium to another did come at the point shown by Pfeiffer's results, and to make sure that the variations in Pfeiffer's data were due to experimental error. On this account I have made no measurements on the end curves, where water and where ester are part solvents, and in the case of ethylisovalerate I have measured only one series. The results are given in Tables XXXVII.–XXXIX.

TABLE XXXVII.

x = c.c. H_2O; y = c.c. Ethylisovalerate; 5 c.c. Alcohol. Temp 20°.

Formula $(x - 0.004\,y)^n\,(y - 0.002\,x) / z^{n+1} = C$; $n = 2.45$; $\log C = \bar{1}.149$.

Water		Et Val.		
Calc.	Found.	Calc.	Found.	log C.
9.98	10.00	0.15	0.15	$\bar{1}.152$
8.05	8.00	0.24	0.23	$\bar{1}.142$
6.01	6.00	0.46	0.46	$\bar{1}.147$
4.99	5.00	0.72	0.72	$\bar{1}.152$
4.00	4.00	1.23	1.23	$\bar{1}.149$
				$\bar{1}.148$

TABLE XXXVIII.

x = c.c. H_2O ; y = c.c Ethylbutyrate ; 5 c.c. Alcohol. Temp. 20°.

Formula $(x - 0.005\,y)^{n_1}\,(y - 0.008\,x)\,/\,z^{n_1+1} = C_1$; $n_1 = 2.44$; $\log C_1 = \bar{1}.449$.

x.		y.		
Calc.	Found.	Calc.	Found.	log C_1.
9.99	10.00	0.34	0.34	$\bar{1}.450$
8.01	8.00	0.51	0.51	$\bar{1}.447$
5.97	6.00	0.95	0.96	$\bar{1}.453$
5.01	5.00	1.45	1.44	$\bar{1}.447$
3.99	4.00	2.46	2.47	$\bar{1}.451$
				$\bar{1}.449$

Formula $(x - 0.005\,y)^{n_2}\,(y - 0.008\,x)\,/\,z^{n_2+1} = C_2$; $n_2 = 1.20$, $\log C_2 = \bar{1}.623$.

				log C_2
2.96	2.96	3.99	4.00	$\bar{1}.624$
2.46	2.48	4.94	5.00	$\bar{1}.628$
2.12	2.10	6.07	6.00	$\bar{1}.618$
				$\bar{1}.623$

TABLE XXXIX.

x = c.c. Water : y = c.c. Isoamylacetate ; 5 c.c. Alcohol. Temp 20°

Formula $(x - 0.012\,y)^{n_1}\,(y - 0.002\,x)\,/\,z^{n_1+1} = C_1$, $n_1 = 3.50$; $\log C_1 = \bar{1}.414$.

x.		y.		
Calc.	Found.	Calc.	Found.	log C_1.
7.00	7.00	0.41	0.41	$\bar{1}.414$
6.00	6.00	0.70	0.70	$\bar{1}.414$
5.01	5.00	1.32	1.31	$\bar{1}.411$
				$\bar{1}.413$

Formula $(x - 0.012\,y)^{n_2}\,(y - 0.002\,x)\,/\,z^{n_2+1} = C_2$; $n_2 = 1.50$; $\log C_2 = \bar{1}.559$.

				log C_2.
3.62	3.61	3.00	3.00	$\bar{1}.558$
3.00	3.01	3.99	4.00	$\bar{1}.560$
2.60	2.60	5.00	5.00	$\bar{1}.559$
				$\bar{1}.559$

Although Pfeiffer does not say so, his amylacetate and ethylvalerate are unquestionably iso- and not the normal compounds. We can now take up the results given in Tables XXXVII.–XXXIX. and see how satisfactorily they fulfil their object. Ethylbutyrate and amylacetate show the change from one equilibrium to the other at the same point that Pfeiffer found. The ethylbutyrate and ethylisovalerate mixtures are perfectly regular at concentrations beyond those used by Pfeiffer, and the isoamylacetate is normal throughout both in Pfeiffer's work and in mine, so that the variations in Tables XXIX.–XXXI. are due to experimental error. The agreement in results between the two sets is shown in Table XL., where I give in the first column the value of the exponential factor $n+1$ from the formula

$$(x - s_1 y)\,(y - s_2 x)^n \,/\, z^{n+1} = C,$$

and in the second column the values for the simplified integration constant log K.

TABLE XL.

Ester.		$n+1$.	log K.
Ethylisovalerate	Pfeiffer	1.40	$\bar{1}.773$
"	W. D. B.	1.41	$\bar{1}.754$
Ethylbutyrate	Pfeiffer	1.41	$\bar{1}.847$
"	W. D. B.	1.41	$\bar{1}.840$
Isoamylacetate	Pfeiffer	1.294	$\bar{1}.893$
"	W. D. B.	1.286	$\bar{1}.870$

As will be seen, the values of $n+1$ are identical, the values for log K, though very close, are not quite the same. This may be due to inaccuracies in the work, but I am more inclined to attribute it to differences in temperature. It is not known at what temperature Pfeiffer worked, and it would take only a slight difference to account for the variation. In Table XLI. I have tabulated the $n+1$ values from Pfeiffer's results, together with log C and log K.

TABLE XLI.

Ester.	$n+1$.	log C.	log K.
Methylisovalerate	1.37	$\bar{1}.807$	$\bar{1}.859$
Ethylisovalerate	1.40	$\bar{1}.682$	$\bar{1}.773$
Ethylisovalerate *	1.41	$\bar{1}.653$	$\bar{1}.754$
Methylbutyrate	1.52	$\bar{1}.888$	$\bar{1}.926$
Ethylbutyrate	1.41	$\bar{1}.785$	$\bar{1}.847$
Ethylbutyrate *	1.41	$\bar{1}.774$	$\bar{1}.840$
Propylbutyrate	1.378	$\bar{1}.651$	$\bar{1}.747$
Ethylpropionate	1.39	$\bar{1}.931$	$\bar{1}.878$
Propylpropionate	1.45	$\bar{1}.733$	$\bar{1}.816$
Ethylacetate *	1.555	....	....
Propylacetate	1.23	0.166	0.135
Butylacetate	1.30	$\bar{1}.912$	$\bar{1}.932$
Isoamylacetate	1.294	$\bar{1}.861$	$\bar{1}.893$
Isoamylacetate *	1.286	$\bar{1}.832$	$\bar{1}.870$
Propylformiate	1.38	$\bar{1}.967$	$\bar{1}.976$
Butylformiate	1.333	0.057	0.043
Isoamylformiate	1.35	$\bar{1}.808$	$\bar{1}.858$

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* My own measurements.

The first thing that strikes one about this table is the way in which so many of the $n + 1$ values approximate to 1.40. Why this should be so is entirely unknown. In the log K values we notice that, for the same acid, increasing the carbon atoms in the alcohol radical diminishes the constant. There is only one exception to this, butylformiate, and here the possible error is very large. It looks also as if the constants might be additive, being made up of one factor for the alcohol and another for the acid radical; but the experimental data is too insufficient to justify this hypothesis. It is very much to be hoped that some one will make a careful series of experiments to settle this point.

Formula II. was deduced for the case when the reacting weights of the substances in equilibrium are not functions of the concentration. The measurements of Pfeiffer and myself show that, with the possible exception of the chloroform-water-acetone series, this condition has been satisfied in all the cases studied, though the experiments extended over a wide range of concentrations. This is in flat contradiction with the determinations of the reacting weights by the boiling-point and freezing-point methods. These methods give accurate results only for very dilute solutions, and even then only for certain solutes in certain solvents. To explain the variations, we are forced to assume "double molecules" in some cases, polymerization with increasing concentration in practically all cases, and "variations from the gas laws." I have brought together a large series of measurements in which there is no sign of any of these things. I see only two possible hypotheses to account for this discrepancy: first, to enunciate a new and most interesting law, to wit, presence of a third substance prevents "polymerization" and "variations from the gas laws"; second, the formula for the change of vapor pressure with the concentration is incorrect. The first hypothesis seems to me out of the question, and there remains only the second. It is a bold thing to question so universally accepted a formula, but I feel convinced that it is not right, and that equal reacting weights of different substances do not produce the same change of vapor pressure. I think that the mistake in the past lay in assuming that the work done in compressing a dissolved substance from the volume V_1 to the volume V_2 by means of a semipermeable piston is equal to $\int p\,d\,v$ between those limits, irrespective of the nature of solute and solvent. I have already collected some experimental evidence in favor of this view, and I hope before long to be able to establish my point.

The facts brought out in this paper throw light on a research by

Abegg * carried out under the direction of Arrhenius. Abegg let alcohol diffuse into a salt solution and found, to his surprise, that the salt, instead of remaining equally divided throughout the liquid, diffused somewhat into the part not yet reached by the alcohol. He concludes that this extraordinary behavior can only be accounted for on the assumption that alcohol increases the osmotic pressure of a dissolved salt. What happens is very simple. When the alcohol has diffused only a little way, one may consider the solution as composed of two parts, one containing a large amount of alcohol, the other very little. The dissolved substance, being in this case less soluble in the first layer than in the second, diffuses into the second only to go back again as the alcohol becomes more evenly divided throughout the liquid. Except that the part containing much alcohol and little water merges insensibly into the part containing much water and little alcohol, and is not in equilibrium with it, the case does not differ from two layers formed by ether and water, where it is well known that the concentration of a third substance is not the same in the two layers. The effect of the alcohol is not, as Abegg assumes, to increase the osmotic pressure of the solute, but to diminish its solubility in that portion of the liquid. If, instead of taking salts which were only slightly soluble in alcohol, Abegg had let water diffuse into water containing in solution some substance very soluble in alcohol, slightly soluble in water, he would have observed the opposite effect, and the dissolved substance would have diffused partially into the layer rich in alcohol.

Another line of reasoning which is not quite defensible is that taken by Wildermann,† in his paper, "Ueber cyclische Gleichgewichte." His train of thought is something as follows. Suppose he has a system of three phases, bromine, a solution of bromine in water, and the vapor of bromine and water, it being assumed that the amount of water which dissolves in the bromine can be neglected. He adds to the aqueous solution some substance which does not dissolve in bromine perceptibly, such as potassium bromide or sulphuric acid. The three phases, when in equilibrium, have still the same concentration of liquid bromine and of bromine vapor. Therefore the solubility of the bromine in the liquid cannot have changed. It does change experimentally; therefore, in order to reconcile the reasoning with the facts, he concludes that the apparent change, decrease or increase, is due to chemical action, and that the amount of bromine dissolved as such remains unchanged. This may be true in the special examples studied

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* Zeitschr. f. ph. Chem., XI. 248. 1893.

† Ibid., XI. 407.

by Wildermann.* That I cannot say; but it is not true that it is a necessary theoretical conclusion, and there is no proof that it is correct in any case. If, instead of adding potassium bromide, we add to the water some liquid in which bromine is readily soluble, the amount of bromine dissolved will increase without there being any reason to assume chemical action in order to account for it. Bromine is not a good substance to consider, because there are so few liquids soluble in water in which it dissolves without decomposition, and also because we cannot ignore the solubility of the added substance in it. Let us rather treat the case when we have iodine instead of bromine. Suppose we have the system, solid iodine, a solution of iodine in water, and vapor of iodine and water; we add alcohol to the solution. The concentrations of the solid iodine and the iodine vapor will remain practically unchanged; therefore the solubility of iodine in the water, and alcohol should remain unchanged according to Wildermann. As a matter of fact it does change, and I do not see how this variation can be attributed to chemical action unless all solution is defined as chemical action, which begs the question though very possibly true. There may be a radical difference between the action of the alcohol and the action of potassium iodide; but that difference has not been shown. As far as I can see, Wildermann's conclusions require that adding alcohol to a saturated salt solution should have no effect on the concentration of the salt because the equilibrium between the solid salt and its own vapor would remain unchanged.

Early in this paper I proposed the word "solute" as something distinct from "solvent," and it is necessary for me to justify that distinction. The usual way of looking at binary solutions is to consider them as mixtures, and that it is purely arbitrary which of the two substances we consider as solvent and which as dissolved substance. The following citations will show what the prevailing opinion at the present moment is.

Lothar Meyer, after pointing out that in alcohol-water mixtures it depends on the nature of the semipermeable membrane which substance exerts the osmotic pressure, says: † "Mit der Beschaffenheit der Membran tauschen beide Stoffe die Rollen; es ist daher eine Willkür wenn wir den einen als gelöst, den anderen als das Lösungsmittel bezeichnen." Ostwald is consistent to the bitter end, saying: ‡

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* See Jakovkin, Zeitschr. f. ph. Chem., XIII. 539. 1894.

† Zeitschr. f. ph. Chem., V. 24. 1890.

‡ Ibid., XII. 394. 1893.

"Lösungsmittel ist derjenige Stoff des Gemenges, welcher bei dem betrachteten Vorgange ausgeschieden wird." This view is heroically logical, for it means that, when a salt crystallizes from a saturated solution, the mother liquor consists of water dissolved in the salt.

Nernst's position on the subject is doubtful. He puts solutions under the head of physical mixtures and remarks:[*] "Die verdünnten Lösingen sind Gemische welche eine Komponente in grossen Ueberschuss zu den übrigen enthalten; erstere bezeichnen wir in diesem Falle als das Lösungsmittel, letztere als gelöste Stoffe." On the other hand, he draws a distinction between freezing out the solvent and crystallizing out the solute.[†] He does not accept the view that the salt is the solvent in a saturated solution; but he does not suggest in any way that there may be different laws for the solute and the solvent. Planck is very clear and precise; he defines dilute solutions in almost the same words as Nernst, and goes on:[‡] "Bei einer beliebigen Lösung kann jeder Bestandtheil derselben als Lösungsmittel oder als gelöster Stoff aufgefasst werden." This means that in a mixture of two liquids either may be considered as the dissolved substance, and will therefore decrease the partial vapor pressure of the other, and this decrease of the vapor pressure will be greater the greater the concentration of the dissolved substance. This is not in agreement with the facts. A saturated solution of ether in water has the same partial vapor pressures as a solution of water in ether saturated at the same temperature.[§] *For the moment we will consider ether as the dissolved* substance. In the first solution, the volume concentration is roughly 10% ; in the second, about 99% at 20° ; and yet this enormous change of concentration has no effect on the partial vapor pressures. The figures are still more remarkable if we consider solutions of chloroform in water and water in chloroform, when one of the components is present in infinitesimal quantities. We must assume one of two things: either that our present formula for the change of the vapor pressure with the concentration is all wrong, since it does not admit of the vapor pressure of one of the components passing through a minimum; or that there is a difference between solvent and solute, and that each has its own law expressing the change of its vapor pressure with the concentration. This time I prefer the second assumption, with all that it implies. The equations of van 't Hoff and Raoult are the rough statements of the laws for the solvent. The corresponding expressions for the solute have not yet been worked out. The distinction between solvent and solute is very clear in solid solutions of metals in metals. Starting from either of two pure metals a depression of the freezing point is noted when the other is added, the two curves thus formed meeting at the melting point of the eutectic alloy. Here there can be no question that along one curve the first metal is solvent, while on the other it plays the role of solute. In the case of two partially miscible liquids there is also no difficulty in determining which is solvent and which solute. When ether and water are shaken together, the upper layer contains water as dissolved substance, the lower ether. With completely miscible liquids having a maximum (or minimum) vapor pressure at some concentration, such as propylalcohol and water (formic acid and water), it is probable that the change of solvent occurs at the concentration corresponding to the maximum (or minimum) vapor pressure. With such things as ethylalcohol and water, which are infinitely miscible and which show no maximum or minimum vapor pressure, it is impossible at present to say at what concentration alcohol ceases to be the solvent and water assumes that duty. As soon as we have worked out the relation between the concentrations in the solution and in the vapor, I feel certain that we shall find that it requires two curves to express the relation, and not one. The intersection of these curves will be the point where the solvent changes. I look upon my own results with ternary mixtures as very significant in this respect, the change from one curve to another coming at the point where the precipitate or the solvent changed. It is interesting to note that at the point, for instance, where an excess of one of the partially miscible liquids first has no effect, the solubility curve of the dissolved substance has a "break." The possibility of such a case has always been denied except by the upholders of the "hydrate theory."

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[*] Theoretische Chemie, p. 115.

[†] Ibid., p. 393.

[‡] Grundriss der Thermochemie, p. 131.

[§] Wied. Ann., XIV. 219, 1881; Ostwald, Lehrbuch, I. 644.

The effect of temperature on the various equilibria will form the subject of a special paper, and I shall reserve for it the discussion of changes of temperature coefficient at the intersections of two curves, one or two very striking instances of which I have come upon incidentally in my work so far. I hope also to be able to present a paper on equilibrium in two liquid layers, a subject which is of especial interest because the theoretical treatment based on the experimental work in this paper gives results which are not in accordance with the assumptions on which Nernst bases his Distribution Law. Besides, there is the application of the Mass Law to the case where one or more of the components is solid, and to the instances where there is an increase instead of a decrease of solubility.

The results of this paper may be summarized briefly as follows.

1. The equilibria between two partially miscible liquids, and a consolute liquid follow the Mass Law.

2. There are four sets of equilibria corresponding to four different series of solutions.

3. If the two liquids are practically non-miscible, there are only two sets of equilibria.

4. The reacting weights of the liquids studied were not functions of the concentration, — possibly with one exception.

5. There is a fundamental difference between the solute and the solvent.

6. The solubility curve of a substance in a varying mixture of two liquids at constant temperature has a break.

XIV.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

A REVISION OF THE ATOMIC WEIGHT OF STRONTIUM.

FIRST PAPER: THE ANALYSIS OF STRONTIC BROMIDE.

By Theodore William Richards.

Presented June 9, 1894.

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Earlier Work.

A glance at published results shows that the atomic weight of strontium has not been investigated for thirty-five years. The early determinations, good enough for their time, show variations which render them quite unsatisfactory to-day; and the case is parallel in every respect to that of barium, which has formed the subject of two recent papers.*

The oldest experiments of any note upon the atomic weight of strontium are those of Stromeyer,† who measured, in 1816, the gas evolved from strontic carbonate upon its decomposition by an acid. The result, which is only of interest historically, gives Sr = 87.3, if a litre of carbon dioxide weighs 1.977 grams under normal conditions.

At about the same time Rose ‡ found that 181.25 parts of argentic chloride could be obtained from a hundred parts of strontic chloride,— data which indicated Sr = 87.31. Twenty-seven years afterward, in

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* These Proceedings, XXVIII. 1; XXIX. 55.

† Schweig. J., XIX. 228; Meyer u. K. Seubert's Atomgewichte, p. 123.

‡ Poggendorff's Annalen, VIII. 189.

1843, Salvetat * determined by loss of weight the carbon dioxide in strontic carbonate, and concluded that the metal must be 88.0, — a result which scarcely improved the situation.

Subsequently, in 1845, Pelouze † found the amount of silver necessary to precipitate a weighed amount of ignited strontic chloride; his results give the value Sr = 87.70. Thirteen years later Marignac ‡ repeated these experiments, determining also the amount of crystal water in crystallized strontic chloride, as well as the amount of strontic sulphate obtainable from the salt. Thus he found that 15.000 grams of crystallized strontic chloride yielded 8.9164 § grams of the anhydrous salt and 10.3282 grams of strontic sulphate; moreover, 15.000 grams of hydrated strontic chloride required 12.1515 grams of silver for precipitation. Another similar series of experiments upon the water of crystallization made its amount appear three milligrams more than before. These data give basis for a number of possible values for the atomic weight of strontium, ranging from 87.17 to 87.55, the individual figures being tabulated below.

In 1859 Dumas ‖ published another determination of the ratio of strontic chloride to silver, the salt having been fused in a stream of hydrochloric acid. Altogether, 27.3435 grams of strontic chloride required in his hands 37.252 grams of silver, the individual values for strontium varying from 87.3 to 87.8. Since this time the subject has remained untouched.

Below is tabulated a list of the various determinations, grouped according to the ratios determined.

The Atomic Weight of Strontium.

Oxygen = 16.000.

From the carbonate:

Stromeyer, 1816	87.30
Salvetat, 1843	88.00

Ratio of strontic and argentic chlorides:

Rose, 1816?	87.31

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* Comptes Rendus, XVII. 318.

† Ibid., XX. 1047.

‡ Liebig's Annalen, CVI. 168.

§ Corrected by L. Meyer u. K. Seubert, Atomgewichte, pp. 78, 79.

‖ Liebig's Annalen, CXIII. 34.

Ratio of anhydrous strontic chloride to silver:

Pelouze, 1845	87.70
Marignac, 1858	87.48
Dumas, 1859	87.53

Ratio of crystallized strontic chloride to silver:

Marignac, 1858	87.52

From the crystal water in strontic chloride:

Marignac, 1858	87.35

Ratio of anhydrous and crystallized strontic chloride to strontic sulphate:

Marignac, 1858	87.2 to 87.6

Selected by Clarke	87.58
Selected by Meyer and Seubert	87.5
Selected by Ostwald *	87.5

A critical review of the list reveals a great lack of trustworthiness in all the figures. The values deduced from the carbonate, and those involving water of crystallization, may all be thrown out at once; and the results yielded by the displacement of hydrochloric by sulphuric acid are but little better. The series upon which most chemists have relied — the one based on the titration of the chloride by means of silver — is hopelessly vitiated by the imperfect execution of the method of analysis.† If any further proof of this uncertainty were needed, the following table, giving a comparison of the work of different experimenters upon other chlorides, would furnish it.

MOLECULAR WEIGHTS OF CHLORIDES BY THE METHOD OF GAY-LUSSAC.

	Pelouze.	Marignac.	Dumas.	Stas.	
				1st.	2d.
NaCl	58.434		58.468	58.506	58.503
KCl		74.539		74.583	74.600
NH_4Cl	53.464	53.450		53.530	53.532

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* Much assistance in preparing this list has been obtained from the well known works of these authors. The figures have all been based upon the most recently accepted atomic weights.

† These Proceedings, XXIX. 80 *et seq.*

Thus, Pelouze, Marignac, and Dumas all obtained low results with the method of Gay-Lussac; in fact, the error sometimes exceeded the tenth of one per cent. The cause of this error, which appeared also in the work of these experimenters upon barium, has already been pointed out in another paper.*

We are thus led to infer that the true molecular weight of strontic chloride must exceed the usually accepted value 158.4 by about one tenth of one per cent, and that the true atomic weight of strontium must be nearly 87.7. This inference is confirmed by the result of the investigation now to be described.

The balance and weights, and the methods of weighing and of tabulating results employed in the work recounted below have already been described in sufficient detail.† The balance seems to have increased slightly in sensitiveness during its four years' work, owing perhaps to the smoothing of microscopic roughnesses in the bearings. It is almost needless to say again that the weights were carefully standardized from time to time, and the small, surprisingly constant corrections were always applied. The correction to the vacuum standard was calculated by the usual formula:

$$\left(\frac{0.001293}{\text{sp. gr. substance}} - 0.000156\right)\frac{H}{760}\,\frac{273^\circ}{273^\circ + t^\circ}$$

$= \text{correction in grams for 1 gram of substance.}$‡

The values thus calculated for the appropriate substances at 20° and 760 mm. were as follows:

Correction to be applied to One Gram of Substance.

	Gram.
Silver	−0.000031
Argentic bromide	+0.000043
Strontic bromide	+0.000141

The general plan of the following work was similar to that adopted in the case of barium. For obvious reasons the bromide of strontium was chosen as the starting point; and the investigation began with a study of the properties of the salt, in order to determine its fitness for the purpose.

The atomic weight of silver is assumed to be 107.93, and that of bromine 79.955, unless a definite statement to the contrary is made.

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* These Proceedings, XXIX. 80.

† These Proceedings, XXVI. 242; also XXVIII. 5.

‡ H = atmospheric pressure; t° = atmospheric temperature at the time of weighing; 0.000156 = standard weight of air displaced by 1 gram of brass.

PROPERTIES OF STRONTIC BROMIDE.

The properties of the bromide of strontium resemble very closely those of the corresponding salt of barium. As is well known, however, the strontium salt usually crystallizes with six instead of with two molecules of water. The crystals, unlike those of the barium salt, are noticeably hygroscopic in ordinary air, so that they cannot be weighed with great accuracy; they melt easily in their own water of crystallization at about 100°. This latter fact renders more difficult the quantitative drying of the salts; indeed, in the few cases where the water of crystallization was determined, it was necessary to allow the crystals slowly to lose their water in a desiccator before ignition. Thus, it was found in the following experiment that five molecules of water were given off, the sixth having very little, if any, tension at ordinary temperatures.

		Grams.
Initial weight of strontic bromide		1.3305
Constant weight after three weeks over H_2SO_4		.9926
Heated to 200° for three hours		.9246
Loss of weight in dry air	Found . .	= 25.41
	Calc. for 5 H_2O	= 25.33
Additional loss on ignition	Found . .	= 5.11
	Calc. . . .	= 5.06

A week's standing in the air of the laboratory sufficed to supply again all the water which had been lost. These results point without doubt to the existence of a definite substance having the formula $SrBr_2 . H_2O$, which is hygroscopic in the air and corresponds to the compound $BaBr_2 . H_2O$, obtained in a similar way.* The existence of this substance has already been inferred by Lescœur † from observations of the vapor tension of the crystal water. Anhydrous strontic bromide is perhaps even more hygroscopic than the corresponding salt of barium.

Strontic bromide melts to a transparent liquid at 630° (Carnelly), losing bromine in noticeable quantities if exposed to the air for some time at this temperature. Fused in a current of dry hydrobromic acid the salt soon recovers this lost bromine, and upon subsequent solution in water shows itself to be wholly neutral both to phenol phthalein and methyl orange. It will be seen that this fact is of the utmost significance. The cold fused transparent or translucent mass is much less hygroscopic than the powder from which it was made.

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* These Proceedings, XXVIII. 12, foot-note.

† Ann. de Chim. et de Phys., [6.], XIX. 553 (1890).

The importance of driving out every trace of water from the salt before weighing cannot be overestimated. Systematic experiments* with baric bromide and chloride led to the conclusion that probably neither of these salts retains water at a red heat, and it was to be expected that the same fact might be true of the substance in hand. In order to test the point, four grams of very pure strontic bromide dried at about 400° were fused in a stream of hydrogen bromide. The mass *gained* nearly six milligrams in weight, showing that the loss of bromine in the air at 400° much more than counterbalanced a possible trace of water. Again, 11.2610 grams of the same specimen, dried at 305° until constant in weight, were found to weigh 11.2630 grams after fusion as before. Since these gains corresponded closely with losses of bromine found alkalimetrically in similarly heated but unfused samples, it is evident that very little if any water can be held by the dried salt. It has already been pointed out that no absolute proof of such a fact is possible;† and these experiments, together with the analogy furnished by the more manageable barium salts, seem to be the last resort. The apparatus used for these experiments will be described under the heading "Method of Analysis."

The specific gravity of anhydrous strontic bromide has been found by Bödeker to be 3.96. Since no more recent data regarding this constant could be found, another determination, described below, seemed to be needed. 3.2560 grams of a pure specimen which had been fused in the air and dried at 200° in the pycnometer were found to displace 0.6678 gram of toluol at 24°. Since the specific gravity of the toluol under these conditions, referred to water at 4°, was found to be 0.8618, that of the strontic bromide referred to the same standard must be 4.203. Again, 2.3065 grams of strontic bromide which had been fused in a stream of hydrobromic acid displaced 0.4699 gram of toluol, thus having a specific gravity of 4.229. The mean of these determinations, 4.216, was adopted as the basis of the reduction of the weighings to the vacuum standard.

Strontic bromide, like baric bromide and chloride, may be evaporated to apparent dryness over a free flame in a platinum dish without losing a trace of halogen. Experiment showed that, upon mixing pure bromide of strontium with small quantities of bromide of calcium and barium and crystallizing the mixture, both impurities tended toward the mother liquors. Hence simple crystallization affords a method of eliminating the two most likely impurities.

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* These Proceedings, XXVIII. 12; XXIX. 58.

† These Proceedings, XXVIII. 14.

The other properties of strontic bromide do not pertain especially to the present work.

PREPARATION OF MATERIALS.

Strontic Bromide. — Six different specimens of the salt were analyzed, in order to establish the presence or absence of accidental impurities.

In the first place, five hundred grams of the purest strontic nitrate of commerce were dissolved in two litres of pure water, and four times in succession a cubic centimeter of pure sulphuric acid, diluted with much water, was added to the solution. Each time only a small amount of precipitate appeared at once, the rest appearing slowly. After waiting in each case three or four days, the clear liquid was decanted. No barium could be found even in the first precipitate of strontic sulphate; but it is true that the spectroscope is not a very satisfactory means for the detection of barium under these circumstances. The acid solution of strontic nitrate, which had been thus almost if not quite freed from a possible trace of barium, was evaporated to small bulk, filtered from the precipitated strontic sulphate, and twice successively brought to crystallization. Each mass of crystals was washed three times with alcohol upon the filter pump, to free it from the mother liquor, which might contain calcium or magnesium.. After having been converted into pure carbonate by precipitation with ammonic carbonate and long continued washing the strontium was combined with bromine. For this purpose hydrobromic acid remaining from the barium work, obtained by repeated fractional distillation of the common acid, was used.

The strontic bromide was evaporated in a platinum dish. This was slightly attacked, bromine having been set free by a little occluded strontic nitrate in the carbonate. After evaporation to dryness the bromide was fused at a bright red heat in platinum. The alkaline solution of the fused cake was treated with hydric sulphide, filtered, acidified with hydrobromic acid, warmed, filtered from the platinic sulphide, boiled to free it from sulphuretted hydrogen, again filtered, and crystallized twice from water. The crystals were washed with alcohol, and the strontic bromide thus obtained is numbered I. below; it was used for the three preliminary experiments, as well as for Analysis 13.

The second sample of strontic bromide was prepared from similarly treated strontic nitrate which had been recrystallized four times instead of twice. The nitrate was converted into oxide by ignition in a nickel crucible; and the dissolved residue was filtered to get rid of a small amount of nickel. Ammonic sulphydrate gave no trace of coloration to a portion of the filtrate. Two recrystallizations in a platinum bottle sufficed to free the strontic hydrate from a trace of undecomposed oxides of nitrogen, and the last crystals dissolved to form an absolutely clear solution in pure hydrobromic acid.* The solution of strontic bromide was evaporated to crystallization, the crystals were dehydrated, and the anhydrous salt was fused; finally, after solution, standing, and filtration, a fresh crop of crystals was obtained. This sample, labelled No. II., was used for Analysis 14.

Among several different methods for obtaining pure strontic salts, that recommended by Barthe and Falières † seemed to promise well and accordingly the third preparation was based upon their work The so called "pure" strontic chloride of commerce was dissolved in water, treated with ammonic hydrate and a little carbonate, and filtered from the precipitate containing iron, aluminum, and so forth. To the filtrate was added an excess of sulphuric acid, and the precipitated strontic sulphate was thoroughly washed with dilute sulphuric acid and then with pure water, in the hope of freeing it from magnesium and calcium. When the wash water became neutral to methyl orange the precipitate was treated with enough ammonic carbonate solution to convert about half of it into carbonate, and the mixed precipitate was then washed with water by decantation until only a very small constant trace of sulphuric acid (due to strontic sulphate) was found in the decantate. The carbonate was then decomposed by pure hydrochloric acid, and the solution was allowed to stand in a glass flask for nine months over the undecomposed sulphate, with occasional shaking. The strontic chloride was decanted, the sulphate was washed once with water, and the filtered decanted liquid was evaporated in a platinum dish until most of the free hydrochloric acid had been expelled. The dissolved residue was neutralized with ammonia, shaken with a little ammonic carbonate, and then filtered. To the greatly diluted filtrate was added an excess of pure ammonic carbonate, and the precipitate was washed until the wash water was free from chlorine. The strontic carbonate was dissolved in nitric acid which had been twice distilled in platinum, and the nitrate was crystallized twice successively in a platinum dish. Each quantity of crystals was washed with small quantities of water and three or four additions of alcohol. The first mother liquor, upon being fractionally precipitated by means of alcohol, showed distinct traces of calcium in the extreme solution; thus Barthe and Falières's method was not capable of freeing the substance wholly from calcium. The second mother liquor showed no trace of calcium upon the most careful scrutiny.

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* See these Proceedings, XXVIII. 17, bottom of page.

† Journ. Chem. Soc., Abs. 1892, p. 1277. Bull. Soc. Chim., [3.], VII. 104.

Two hundred grams of the purest crystals, after having been dried at 130°, were dissolved in about a litre of the purest water and filtered into a large platinum dish, into which was passed first pure ammonia gas and then pure carbon dioxide through a platinum tube.* The pure strontic carbonate was washed by decantation eight or ten times, dried on the steam bath, and ignited in a double platinum crucible over a spirit lamp.

Part of this carbonate was converted into bromide by means of the purest hydrobromic acid,† and the product was digested for a long time with a considerable excess of carbonate. After filtration and evaporation the strontic bromide was fused in a platinum dish over the spirit lamp, the salt being perfectly clear while liquid. The translucent cake was dissolved, allowed to stand, filtered, faintly acidified with hydrobromic acid, and crystallized twice from water. Each time the crystals were washed with the purest alcohol. The resulting bromide of strontium was used for Analyses 1, 2, 3, 5, 6, 7, 12, 15, 16, 17, and 18.

The next sample was prepared from the strontic carbonate which had been digested with the strontic bromide just described. It was dissolved in the purest hydrobromic acid and purified much as before, except that the salt was fused twice with intermediate crystallizations, instead of only once. This fourth preparation was used for Analysis 9.

The fifth sample was made by the repeated crystallization of the combined mother liquors obtained from the four previous preparations. It was used for Analyses 4, 8, and 19.

The sixth preparation of strontic bromide was made from the strontic sulphate remaining from the third. This residue was treated with enough ammonic carbonate to convert all but about twenty grams of the sulphate into carbonate. The washed strontic carbonate having been dissolved in a slight excess of hydrochloric acid, the residual sulphate was allowed to remain in the solution for a week. After filtration, evaporation to dryness in platinum, solution, a second filtration, treatment with a little ammonic hydrate and carbonate, and yet another filtration, the strontic chloride was converted into carbonate by means of purified ammonic carbonate.* After a very complete washing the strontic carbonate was dissolved in pure nitric acid in a platinum dish. The nitrate was crystallized, dried at 150°, recrystallized, washed with alcohol with the aid of the pump, dried, dissolved, and stirred with a little pure strontic carbonate for a week. The filtrate containing pure strontic nitrate was diluted, brought to boiling in a platinum dish, and poured in a fine stream into a boiling solution of pure ammonic oxalate † also contained in platinum. The strontic oxalate was washed with the purest water upon the filter pump, until no ammonia could be detected upon boiling the filtrate with sodic hydroxide. Nessler's reagent still showed a trace of ammonia; but since this could easily be expelled by ignition, and the precipitate was very hard to handle, the washing was not carried further. After drying and powdering, the oxalate was converted into carbonate by ignition at a full red heat. The product was now ground in a mortar with an equivalent amount of pure ammonic bromide,‡ and the whole was gently ignited in a large platinum dish until no more ammonia was evolved. The hundred grams of strontium bromide thus obtained formed a pure white translucent cake upon fusion in a large platinum crucible. The cake was dissolved in water, and the alkaline solution, after having been boiled for some time, was neutralized with sulphuric acid. The clear filtrate from the strontic sulphate was now evaporated to a volume of about a hundred and twenty cubic centimeters, and diluted with two hundred cubic centimeters of the purest alcohol. The mixture was allowed to stand for a day, in order that the strontic sulphate and any trace of baric sulphate which might remain should be precipitated, and then filtered. After three successive crystallizations from water, the substance was used for Analysis 10; a further crop of crystals from the purest mother liquor served for Analysis 11.

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* See page 379.

† Prepared from pure baric bromide and redistilled many times. See these Proceedings, XXVIII. 17.

Considering the pains taken in the purification of even the least pure sample, it is not surprising that all of these samples gave quantitative results which proved them to be essentially identical.

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* See page 379. † See page 379. ‡ See page 380.

Silver. — The preparation of pure silver has been repeatedly detailed. The most elaborate method described in the paper upon barium was used in the present case.[*] A few improvements were introduced, notably the purification of the sodic hydrate used for the reduction of the argentic chloride by means of a strong galvanic current, instead of by hydrogen sulphide. Little but iron was found in it, however. The final crystals of electrolytic silver were usually fused upon pure sugar charcoal or lime, in a reducing flame; once however (for Analysis 10) the crystals contained in a lime boat within a stout porcelain tube were fused in a Sprengel vacuum by means of a Fletcher furnace. Two holes bored through the furnace at right angles to the flame entrance served to admit the tube. The heat was very gradually applied, and after the silver had been melted all the apertures of the furnace were closed and the tube was allowed to cool very slowly. A wide glass tube set into the porcelain tube on one end served as a convenient window for the observation of the fusion.

Ammonic Carbonate. — Two varieties of ammonic carbonate were used for the work just described. The first consisted of ordinary pure "ammonic carbonate," which had been dissolved, treated with a small amount of a pure strontium salt, and filtered. This treatment undoubtedly removed any substance which could seriously interfere with the preliminary purifications for which this ammonic carbonate was used. For the final stages of the purification of the strontium preparations, ammonic carbonate was made by saturating the purest water in a platinum vessel with ammonia gas obtained by boiling the pure strong ammonia of commerce, and then passing into this saturated solution pure carbon dioxide. This latter gas was prepared by the action of dilute nitric acid on marble; it was purified by passing through washing flasks containing water and a meter of glass tube packed with moist beads. Upon delivering the gas into a Bunsen flame, no trace of calcium could be detected spectroscopically. Both gases were conducted into the solution through a platinum tube made for the purpose. The resulting ammonic carbonate undoubtedly contained more or less of the amines common in ordinary ammonia, but it could not have contained a trace of non-volatile impurity capable of contaminating the strontic carbonate for whose preparation it was designed.

Ammonic Oxalate. — This salt was made by neutralizing pure ammonia water with pure oxalic acid, which had been still further purified by many recrystallizations from hydrochloric acid and water. The ammonic oxalate was crystallized twice in a platinum dish, the crystals being thoroughly washed each time. The salt was wholly free from chlorine.

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[*] These Proceedings, XXIX. 64, 65.

Ammonic Bromide was prepared in the usual fashion from ammonia prepared in platinum and bromine purified according to Stas. The reaction was naturally conducted in a flask of hard glass; but the crystallization was carried on as usual in platinum. A slight excess of the pure white substance precipitated 3.97970 grams of argentic bromide (fused, reduced to the vacuum standard) from a solution containing 2.28616 grams of pure silver. From this experiment $AgBr : Ag = 100 : 57.4455$. Stas found 57.445, hence the purity of the ammonic bromide is proved.

A very simple and convenient platinum condenser was used for the preparation work described above. The tube, almost a centimeter in diameter and perhaps twenty-five centimeters in length, is bent, somewhat contracted near one end, and surrounded with a condenser jacket. It is easy to draw out the neck of a round-bottomed flask to fit outside of the conical end, and if the juncture is not absolutely tight a thin film of condensed liquid soon makes it so. If the glass neck be prolonged somewhat above the point of juncture, evaporation from this film is very slow. Of course pure filter paper may be used to tighten the joint if water is to be distilled. The apparatus has the great advantages of cheapness and transparency over the ordinary platinum still. All the hydrochloric, hydrobromic, sulphuric, and nitric acids, water, and alcohol used in the important stages of the work were distilled with the help of this contrivance.

Platinum vessels have been used wherever it was possible to use them in the work detailed above, although the fact is not always mentioned. They were cleaned in the usual fashion.

METHOD OF ANALYSIS.

As in the case of baric bromide,* the silver required to precipitate all the bromine in strontic bromide was determined, as well as the amount of argentic bromide formed by the precipitation.

The chief problem which presented itself was the preparation of pure dry neutral bromide of strontium for weighing. In preliminary analyses the salt was ignited or fused in a platinum crucible, and weighed as the baric bromide had been. The decomposition of the salt was so great, however, that the uncertainty of the alkalimetric correction sometimes amounted to two or three tenths of a milligram; hence this method was clearly inadmissible.

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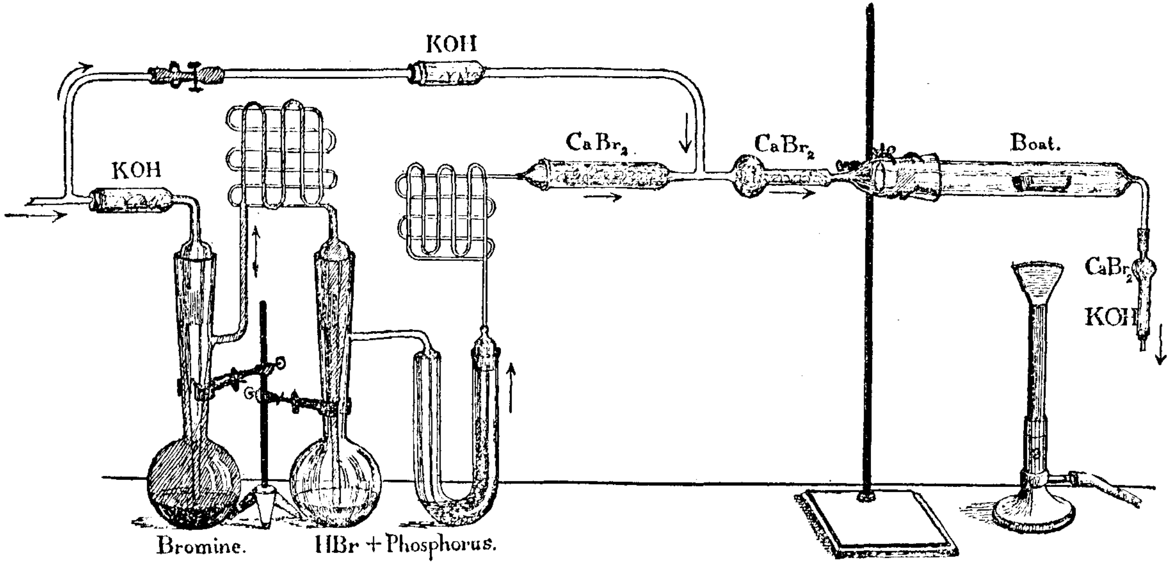
* These Proceedings, XXVIII. 23.

The fusion of the salt in a platinum boat in a stream of nitrogen gave much better results, and two or three further preliminary determinations by this method gave promise of much greater accuracy. It is probable that the slight decomposition which occurred even in the atmosphere of nitrogen was due to the presence at 250°–300° of a slight trace of moisture.

The presence of an excess of hydrobromic acid must necessarily lessen or prevent this decomposition; hence in three succeeding determinations (Nos. 13, 14, 15, below) pure dry hydrogen bromide was added to the nitrogen in which the combustion was conducted.

In these cases, however, the platinum boat, which had previously remained quite constant in weight, was evidently attacked, since upon one occasion (Exp. 15) it lost over two tenths of a milligram, and the pure white strontic bromide became tinged with a brown color. The weight of the boat *after* each fusion was taken as the true weight, because the bromide of platinum, if formed, must precipitate nearly as much silver as the bromide of strontium.

In order to avoid the corrosion of the boat, hydrogen was added in small quantities to the mixture of gases. This, by preventing the dissociation of the hydrobromic acid, effectually preserved the platinum, and the boat remained constant in weight. The pure translucent or transparent colorlessness of the fused salt left nothing to be desired. A somewhat complex piece of apparatus was needed for the purpose. (See page 382.) A mixture of six volumes of pure nitrogen (made by passing air and ammonia over red-hot copper) and one volume of pure hydrogen was delivered from a gas holder through a succession of tubes of red-hot copper, dilute chromic and sulphuric acids, concentrated alkaline pyrogallol, and fused potash, into the arrangement for preparing hydrobromic acid. This, as well as all the apparatus following, was without rubber connections, the ground joints being made tight by means of syrupy phosphoric acid (Morley) and flexible by means of fine glass gridirons (Finkener). The pure dry nitrogen and hydrogen were led in the first place into a flask containing bromine, and then over asbestos and red phosphorus saturated with pure fuming hydrobromic acid. The bromine and hydrobromic acid were proved to be pure by the usual quantitative analysis, and the red phosphorus was ground and washed many times with pure water to



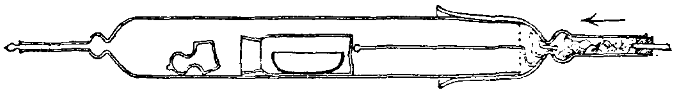
Apparatus for fusing Strontic Bromide.

Pure dry nitrogen and hydrogen enter the apparatus through the tube at the left. The arrangement for preparing this mixture is not shown. Upon closing the pinchcock in the upper left hand corner, the gases are driven through the flasks and charged with dry hydrobromic acid; upon opening the pinchcock, the hydrostatic pressure below causes the gases to flow through the upper short-cut tube and effectually sweep out the acid from the fusion tube. This latter tube, containing the boat in which the strontic bromide is fused, is at the right of the figure.

free it as much as possible from chlorine (Stas). The mixture of pure slightly moist hydrogen bromide, nitrogen, and hydrogen was now dried by calcic bromide free from chlorine and iodine, and thus became ready for use.

The hard glass tube used for heating the platinum boat containing the strontic bromide was ground very tightly into its socket of soft glass, since it was not advisable to risk the presence of phosphoric acid here. The powdered nearly anhydrous strontic bromide, having been packed tightly into the boat and carefully pushed into position in the fusion tube, was thoroughly dried at 200° in a stream of pure air. The elaborate apparatus for preparing the mixture of gases was now connected with the fusion tube, and when all the air had been expelled the boat was slowly heated to cherry-redness until the strontic bromide was wholly fused. The temperature was then allowed to fall a little below 600°, and the solidified bromide of strontium was freed from any possible excess of hydrobromic acid by a current of dry hydrogen and nitrogen free from acid, delivered through a short-cut tube (see page 382).

The almost red-hot boat was now transferred as quickly as possible to the light weighing bottle, within which it was allowed to cool. In the preliminary work (and in Analyses 13 and 14) this bottle was stoppered at once and cooled in an ordinary desiccator. Subsequently an improved desiccator was devised for this purpose. A wide glass tube capable of containing the weighing bottle was drawn out at one end to a fine tube, which was fitted with a ground-glass stopper. The other open end was made slightly conical and ground into a receptacle which was in its turn attached to a drying tube containing fused potash. The following sketch supplements this description.



While the boat was still hot within the fusion tube, the stopper of the weighing bottle was placed in the horizontal desiccator tube. The moment after the transference of the boat into the bottle, both together were slid into the momentarily opened desiccator tube by means of a glass rod which projected from the receptacle. The bottle was held by means of a glass carriage during this manipulation.

The open weighing bottle, with its stopper and fused contents, could now be heated indefinitely in a current of pure dry air at any temperature below the softening point of soft glass. At the moment when it was desired to close the bottle, it was only necessary to elevate the desiccator tube from the horizontal to the vertical position, and the hot stopper fell automatically into the equally hot bottle. The desiccator tube was now closed above, and allowed to cool at least four hours in the balance room. It is needless to say that before taking the final weighing of the bottle its stopper was loosened.

Having thus obtained as nearly as possible the true weight of the typical salt of strontium, the remainder of the analysis was conducted in a manner essentially similar to that adopted in the case of baric bromide.* Since it is unnecessary to describe again most of the precautions, nothing will be noted below excepting those particulars in which the details of the work differed from those already given. Two analyses, which were vitiated by known errors, are omitted from the tables.

THE RATIO OF SILVER TO STRONTIC BROMIDE.

First Series.— In this series a slight excess of silver was taken, dissolved, and diluted with at least a hundred times its weight of water, and added to the strontic bromide in a glass-stoppered flask. After the usual long continued shaking, the precipitate was collected upon a Gooch crucible, and the excess of silver in the evaporated filtrate and first five or six wash waters was determined after Volhard's method.† Upon subtracting this small excess of silver from the total, the amount corresponding to the strontic bromide remains. This method is not a very satisfactory one, the final result being probably too low, because of loss of a portion of the slight excess of silver.

Second Series. — Here the end point of the reaction was determined by titration after the method of Abrahall,‡ very weak solutions of silver and hydrobromic acid being used to titrate backwards and forwards. The mean reading was taken in each case, and the method of procedure resembled exactly the work with barium. These results are much more trustworthy than the last. In several cases the sample of strontic bromide was first analyzed by this method, and subsequently an excess of silver nitrate was added and the preceding method was applied.

Third Series. — For this series a new method was devised. According to Stas,* argentic bromide is wholly insoluble in water; according to Goodwin,† it is only very slightly soluble; while according to Kohlrausch and Rose,‡ it is soluble to the extent of three tenths of a milligram in a litre. The time during which chloride of silver is shaken makes an enormous difference in the solubility, and it is not impossible that a similar effect may occur here. Perhaps Kohlrausch and Rose did not agitate their precipitate so thoroughly as Stas did. According to the present experience the purest silver bromide was capable of yielding a filtrate which would give a very faint opalescence with both silver and hydrobromic acid; and this effect usually diminished upon long continued agitation. The method of determination used in this series was based upon this fact. Somewhat less silver than the amount required was added to the strontic bromide, and a very weak standard solution of argentic nitrate (the cubic centimeter contained a milligram of silver) was dropped in until equivalent solutions of silver and hydrobromic acid produced equal opalescence in two similar pipetted portions of the supernatant liquid. Since the opalescence was so faint that one could only with difficulty see it at all under ordinary conditions, a piece of apparatus, which may be named a "nephelometer" (νεφέλη, a cloud), was devised for detecting it. Two test tubes, holding each just thirty cubic centimeters, were arranged in a wooden frame so that two centimeters of the top of the tubes were in darkness. The bottoms of the tubes were fitted into the top of larger opaque tubes containing water, and were provided with closely fitting cylindrical shades, which could be raised or lowered independently over a graduated scale. All these contrivances prevented disturbing side reflections from the meniscus at the top of the tube and the rounded glass at the bottom. The two test tubes were slightly inclined towards one another, so that the eye at a distance of eight inches could look directly into both without change of position. Filled with pure water the tubes appear absolutely black, even when exposed to a strong light; but an absurdly small amount of precipitate, which no ordinary means

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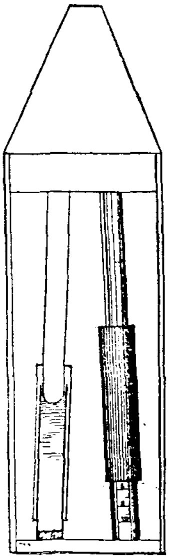
* These Proceedings, XXVIII. 24.

† These Proceedings, XXIX. 66.

‡ These Proceedings, XXVIII. 24.



NEPHELOMETER.

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* Mém. de l'Acad. Belg., XLIII., Part II. Introduction.

† Zeitschr. f. phys. Chem., XIII. 645.

‡ Ibid., XII. 234.

could discover at all, makes a very evident cloudiness. By sliding the shades up and down a point may be found where the two tubes, containing solutions of different cloudiness, appear equal in depth of tone. The reason of this is that only the portion of the opalescence is visible upon which light is allowed to fall. Of course the intensities of the opalescence, and hence the quantities of precipitate, are then inversely as the length of the lighted portions of the two tubes.

If care is taken to direct the light horizontally upon the tubes, considerable accuracy may be obtained with the apparatus, especially if the columns are nearly equal in cloudiness.

A pointed blackened roof with a small hole in the top for the eye is useful in excluding light from the surface of the liquid, thus rendering the comparison easier. The chief advantages of the apparatus lie in the facts that the two disks of light to be compared remain equal in size throughout the comparison, and that the eye is not confused by bright surface reflections. Two typical test series are given below. In each case one shade was adjusted at ten centimeters, and the other was run backward and forward until apparent similarity was obtained.

(*a.*) One tube contained 0.010 milligram of silver, and the other 0.0125 milligram, measured by means of a very dilute standard solution. Both amounts were made up to twenty-five cubic centimeters, and one cubic centimeter of hundredth normal hydrochloric acid was added to each. The opalescence in each was then compared after a thorough stirring and a short delay.

HEIGHTS OF COLUMNS APPEARING ALIKE.

	Stronger Solution.	Weaker Solution.
	8.7 cm.	10.0 cm.
	7.9 "	10.0 "
	6.9 "	10.0 "
	7.6 "	10.0 "
	8.4 "	10.0 "
	8.6 "	10.0 "
	8.9 "	10.0 "
Found,	8.1 cm.	10.0 cm.
True value,	8.0 "	10.0 "

(*b.*) In a similar experiment one tube contained 0.025 milligram of silver, the other 0.0225 milligram.

HEIGHTS OF COLUMNS APPEARING ALIKE

	Stronger Solution	Weaker Solution
	8.8 cm.	10.0 cm.
	8.9 "	10.0 "
	8.2 "	10.0 "
	9.5 "	10.0 "
	8.9 "	10.0 "
	8.7 "	10.0 "
	8.9 "	10.0 "
	9.4 "	10.0 "
Found,	8.9 cm.	10.0 cm.
True value,	9.0 "	10.0 "

Some series were more accurate, others less so, than these, which serve to give a fair idea of the probable error of the method.

The details of the analysis must be evident from what has been said. The method is similar to Stas's third method for the determination of chlorine,* except that of course the opalescence is very much fainter.

Below are given the tables containing the data and results of the three series; these will be comprehensible without further remark.

RATIO OF STRONTIC BROMIDE TO SILVER

First Series. Volhard's Method.

No. of Analysis.	No. of Specimen	Weight of Strontic Bromide taken.	Total Weight of Silver taken.	Excess of Silver	Weight of Silver corresponding to Strontic Bromide.	Ratio $\frac{SrBr_2}{Ag_2}$	Atomic Weight Sr
		grams		m. g			
1	III.	1.49962	1.30893	1.38	1.30755	114.689	87.658
2	III.	2.41225	2.10494	1.43	2.10351	114.677	87.633
3	III.	2.56153	2.23529	1.72	2.23357	114.683	87.645
4	V.	6.15663	5.3686	0.2	5.3684	114.683	87.644
		12.63003			11.01303	114.683	87.644

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* See these Proceedings, XXIX 86.

RATIO OF STRONTIC BROMIDE TO SILVER.

Second Series Abrahall's Method

No of Analysis	No of Specimen.	Weight of Strontic Bromide taken.	Weight of Silver required	Ratio $\frac{SrBr_2}{Ag_2}$	Atomic Weight of Strontium.
		grams.	grams.		
5	III.	1 49962	1.30762	114.683	87.645
6	III.	2.41225	2.10322	114.693	87.667
7	III.	5.24727	4.57502	114.694	87.668
8	V	6 15663	5.3680	114.691	87.663
		15.31577	13.35386	114.692	87.663
Third Series. New Method.					
		grams.	grams.		
9	IV	2.9172	2.5434	114.697	87.675
10	VI	3.8946	3.3957	114.692	87 665
11	VI.	4.5426	3.9607	114.692	87.664
12	III	5.2473	4.5750	114 695	87.671
		16 6017	14.4748	114.694	87.668

RATIO OF ARGENTIC TO STRONTIC BROMIDE.

In many of the preceding determinations the bromide of silver resulting from the decomposition was weighed. In every case a slight excess of silver nitrate was added, to render the argentic bromide wholly insoluble in the filtrate. The very slight amount which may have been dissolved by the wash water during its brief contact with the precipitate was not considered. The precipitate was collected upon a Gooch crucible; and the traces (0.04 to 0.2 milligram) of asbestos carried through were collected upon a small washed filter, ignited separately, weighed, and added to the gain in weight of the crucible. From this was subtracted the loss in weight of the precipitate upon fusion in a covered porcelain crucible. A description of the dark room used for the experiments, and many other precautions and details, will be found in other papers.* The results are tabulated below.

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* These Proceedings, XXVIII. 24; XXIX. 74.

RATIO OF STRONTIC AND ARGENTIC BROMIDES

First Series.

No of Analysis	No of Specimen.	Weight of Strontic Bromide taken	Weight of fused Argentic Bromide found	Ratio $\frac{SrBr_2}{2\ AgBr}$	Atomic Weight of Strontium
		grams	grams		
13	I.	1 6086	2 4415	65 886	87 669
14	II	1 8817	2 8561	65 884	87 662
15	III	4 5681	6 9337	65 883	87 657
		8 0584	12 2313	65 8834	87 660
Second Series					
		grams	grams		
16	III.	1 49962	2 27625	65.881	87 652
17	III	2 41225	3 66140	65 883	87 660
18	III	2 56153	3 88776	65 887	87 674
19	V	6 15663	9 34497	65 882	87 654
		12 63003	19 17038	65 883	87 659

It remains only to bring together the results into one table.

FINAL AVERAGES

Oxygen = 16.000

			Strontium equals
I.	2 Ag : $SrBr_2$	First Series	87.644
II.	" "	Second Series	87.663
III.	" "	Third Series	87.668
IV.	2 AgBr : $SrBr_2$	First Series	87.660
V.	" "	Second Series	87.659
		Total average	= 87.659
		Average, rejecting I. above	= 87.663

The last average is probably most nearly correct.

The analysis of strontic chloride has already been begun, and the preliminary results indicate that the results given above are certainly not too high. For the present, then, the atomic weight of strontium may be taken as 87.66 if oxygen is 16.00, 87.44 if oxygen is 15.96, and 87.01 if oxygen is 15.88.

XV.

ON THE ELECTRICAL RESISTANCES OF CERTAIN POOR CONDUCTORS.

By B. O. Peirce.

Presented October 10, 1894.

Since the subject of electricity began to be studied seriously, many experimenters have made lists of substances arranged in the order of their electrical conductivities. These lists have not agreed with one another in all respects; but at one end of every one of them metals have stood, and at the other end such insulating substances as ebonite, glass, paraffine, shellac, and mica. Somewhere between these extremes have appeared the so called "half-conductors,"* like wood and some kinds of stone. How these latter are to be classed depends very much, of course, upon the uses to which they are put. For work with the small charges and high potentials of experiments in electrostatics, we must generally consider wood as a conductor; while, for practical purposes, we may regard the wooden base upon which a telegraph instrument is mounted as a perfect insulator.

In making electrical measurements in the laboratory, it is often necessary to be able to change quickly the connections of one's apparatus, and for this purpose some kind of "switch-board" must generally be provided. Sometimes a dry wooden board, into which holes have been bored to form mercury cups, will suffice; sometimes a plate of ebonite or a non-combustible slab of slate or marble is required.

I have been obliged, during the last three years, to procure several hundred more or less complicated switch-boards, and many of these had to be used in making accurate measurements of electrical quantities. It has been necessary, therefore, to determine under what circumstances hard dry wood or red vulcanized fibre may safely be used, and when marble or ebonite, or even a block of freshly scraped paraffine, is required. For use with these switch-boards I have provided several hundred resistance coils of German silver, platinoid, and manganine wire, wound on spools two inches in diameter over all, and from four to eight inches long. The coils are furnished with stout copper terminals (Figure 1), and are protected by cylindrical shields made of brass or pasteboard tube. The copper terminals are screwed, with axes parallel to each other, and one inch apart, into one end of each spool. Spools and shields together act as shunts to the coils, and it has been necessary to determine a lower limit for the resistance which such a shunt could offer in practice. It has been necessary also to measure the insulation resistance between the two mercury cups, on a switch-board, into which the terminals of one of the resistance coils dip. These cups are formed by holes three eighths of an inch in diameter (Figure 2), and five eighths or three quarters of an inch deep. The axes of each pair of holes are one inch apart. The holes are bored, or drilled, in a lathe, in the top of the switch-board, with a Förstner bit if the material be wood or vulcanized fibre or ebonite, with a flat or twist drill moistened with water if slate or marble be used.

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* Du Moncel, Annales de Chimie et de Physique, [5.], X. 1877; Addenbrooke, Muir and Jamieson's Pocket-Book, p. 194.

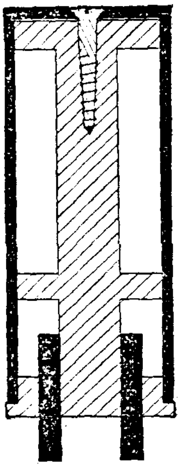

FIG. 1.

In order to get such information as I needed with respect to the insulation resistance which might safely be counted on in the case of wood, marble, or vulcanized fibre, used for the purposes just described, I made a long series of measurements, with the help of a battery of twelve dry cells, and an absolutely calibrated high-resistance mirror galvanometer, on a large number of specimens. Of course individual measurements of this sort have little general value, but a large number of experiments on different samples of material of a given kind make it possible to set a lower limit to the resistance of this substance when used in a given way, and such knowledge as this is often useful when one is planning apparatus. For instance, my experience seems to show that it is perfectly safe to assume that the specific resistance per cubic centimeter of an inch-thick slab of pure white Vermont marble, which has been standing exposed to the air in a fairly dry room for three weeks, is not less than 10^9 ohms, and is probably as much as 10^{10} ohms. Really dry white marble has a far higher specific resistance than this. It is safe also to set a lower limit for the specific resistance of sea-

FIG. 2.

soned wood of a given kind, but only in the sense that wood of resistance as high as this can always be obtained without difficulty in the market. Abnormal specimens occur. In measuring the insulation resistances between the copper terminals of unparaffined maple and birch spools, like or similar to the one represented in Figure 1, I experimented upon a large number of spools which had been lying for about a year in a certain dry closet. The smallest resistance in any case was 1,100 megohms, and the average resistance was more than 2,000 megohms. This is what one may expect to get in spools of this kind. In the same closet were some spools of a different lot, bought of the maker of the other spools, and in no way different in appearance from them. These also had been seasoning beside the others for a year, yet the average insulation resistance of these spools was only a little over one megohm. This is an extreme case. The nearest approach to it that I found in experimenting on other lots of spools was that of some which had been standing for a long time in the damp basement of the laboratory, and represent what the ordinarily good dry spool might become if it were placed for months in a moist place. Yet the lowest resistance in the case of these spools was more than 100 megohms.

It is, of course, well known that the insulation resistance of a porous half-conductor depends very much upon the amount of moisture which it contains, and that this moisture may give rise to all manner of anomalies, as Du Moncel has shown. Thus, white marble when it comes from the mill is often a fairly good conductor, owing to the water which it has absorbed in the process of manufacture, but a fortnight's drying in the sun sometimes increases its resistance ten thousand fold. It is now almost always possible to get kiln-dried wood, and after wood or marble has once been thoroughly dried, an immersion in a bath of hot paraffine tends to prevent the reabsorption of moisture. Red vulcanized fibre absorbs hot paraffine greedily; but I do not think that it would be easy to saturate a piece of fibre so thoroughly with paraffine that a drop of water allowed to rest on its surface for a few moments would not begin to raise a blister.

Prolonged immersion in clean, hot, melted paraffine always increases the insulation of a half-conductor, even if the bath leaves no perceptible coating on the outside. This increase, however, is very slight in the cases of some close-grained substances like rosewood, though it may amount to three or four times the original resistance in the case of a porous conductor. If while such a conductor is immersed in hot paraffine the bath and its contents be placed under the receiver of an air-pump, and the air be alternately exhausted from and re-admitted to the receiver, the resistance of the conductor is always materially increased. This process is in common use for the purpose of improving the insulation between the layers of covered wire in galvanometer coils. A coat of shellac, when not thoroughly dry, often lowers very much the insulation resistance of a porous half-conductor.

The following table shows the results of measurements of the resistance between the two members of each of a large number of pairs of mercury cups of the size shown in Figure 2 bored in the tops of slabs of different substances. The specific resistance of wood for currents going across the grain is generally from 20 to 50 per cent higher than for currents going with the grain. The figures given below may be taken as referring to currents going with the grain. I procured, wherever I could conveniently, a number of pieces of seasoned wood of each variety named, rejecting none, and I believe that the numbers in the table represent fairly what one may expect in practice. The number in the second column of the table, in the same horizontal line with the name of a substance, shows how many pairs of mercury cups bored in slabs of this substance were experimented on, while the numbers in the next two columns give in megohms the lowest and the average resistance between the members of these pairs. Sometimes a single pair of cups only was bored in a slab, sometimes two or three. The resistances between the members of pairs of mercury cups bored in the single specimens of cypress and maple that I had were, in the average, upwards of 2,000 megohms.

TABLE I.

Substance.	No. of Pairs of Cups.	Lowest Resistance in Megohms.	Average Resistance in Megohms.
Ash	13	550	920
Cherry	15	1100	4000
Mahogany . . .	14	430	730
Oak	17	220	420
Pine	24	330	630
Hard Pine	8	10	48
Black Walnut . .	30	1100	3000
Red Fibre	6	2	4

Choice pieces of wood of each of the seven kinds named in the table would yield insulation resistances far higher than those given in the column of averages, and not less than 1,000 megohms even in the case of hard pine.

TABLE II.

Substance.	Lowest Specific Resistance in Megohms found among the Specimens tested.	Average Specific Resistance in Megohms of the Specimens tested.
Ash	380	700
Cherry	2800	6000
Mahogany	310	610
Oak	1050	2200
Hard Pine	17	1050
White Pine . . .	360	1470
Black Walnut . .	320	2100
Vulcanized Fibre .	3	60
Slate	184	280
Soapstone	330	500
White Marble . .	2000	8800

Table II. gives the results of a great number of experiments upon the electric resistances of slabs of different substances, through which currents were sent by means of mercury electrodes placed opposite each other. Each electrode was contained in a cavity excavated in a piece of ebonite (Figure 3), and was generally about 60 square centimeters in area. Comparative measurements made with slabs of wood cut across the grain were rather unsatisfactory, for the reason that there seemed to be in every case a resistance of contact (*Uebergangswiderstand*) at the common surface of the mercury and wood, and the magnitude of this resistance depended very much upon the roughness or smoothness of the cut, and was sometimes greater than the intrinsic resistance of the wood. In experiments made with currents sent across the grain of the wood through slabs of different thicknesses cut from the same plank, the resistances seemed to follow

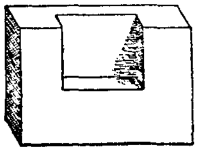

Fig. 3.

Ohm's law so nearly that the contact resistances were of comparatively small importance. The contact resistance between two pieces of wood pressed together seemed to be great, since the insulation resistance of a compound slab formed of two in close contact was far greater than the sum of the resistances of the two taken singly. To avoid any disturbing effects that might arise from injury to the substance at tool-cut edges, slabs were sometimes used (see the shaded portion of Figure 4) much greater in area than the electrodes, and this necessitated the making of allowances (based on experiments with zinc electrodes in a tank of solution of zinc sulphate) for the effect of the spreading of the lines of flow in the slab. This process was not entirely satisfactory, but the results are doubtless quite accurate enough for the purpose in view. The mercury electrodes were effectively insulated from the brass clamping bolts by the intervening slabs of ebonite.

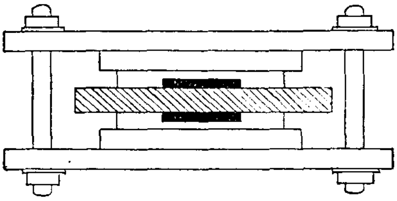

FIG. 4.

All the slabs of stone were specially dried in the summer sun for about three weeks before they were experimented on. Through the kindness of Messrs. Bowker, Torrey, & Co. of Boston, I was enabled to test the specific resistances of a large number of pieces of colored marble of different kinds. A vein in a piece of marble used as a switch-board has been known to short-circuit a fire-alarm system, and it was to be expected that the specific resistances of most colored marbles would prove to be less than that of white marble. In one instance, the specific resistance was as low as three megohms. The single piece of sandstone which I had at my disposal had been in a dry place in the laboratory for more than five years; its specific resistance was thirty megohms. The average specific resistance of hard pine as given in Table II. means little. I have seen a piece of this wood with a specific resistance as high as 4,000 megohms; but very resinous pieces of hard pine, however long they may have been dried, seem to have low specific resistances. Some thin birch, of the kind now used to separate from each other the successive plates of one or two forms of storage cell, had a specific resistance, when dry, of about 500 megohms.

JEFFERSON PHYSICAL LABORATORY,
August, 1894.

XVI.

CONTRIBUTIONS FROM THE CRYPTOGAMIC LABORATORY OF HARVARD UNIVERSITY.

XXIV.—VARIABILITY IN THE SPORES OF UREDO POLYPODII (PERS.) DC.

By B. M. Duggar.

Presented by W. G. Farlow, October 10, 1894.

Different opinions have been held as to the specific importance of certain forms of *Uredo* occurring on various genera of ferns. Likewise an uncertainty has existed relative to the twofold nature of the spores found in a single pustule. With a considerable amount of material representing several host-genera, to which I have had access through the kindness of Dr. Farlow, it has seemed of interest to give the subject careful study, hoping thereby to reconcile some of the views expressed.

Winter* has referred to *Uredo Polypodii* (Pers.) DC. all of the Uredo forms reported on many genera of ferns, the spores of this species measuring 19–52 × 12–22 μ. He distinguishes, however, a *forma Phegopteris,* on *Phegopteris,* based on the more or less polygonal character of the rather larger spores. Schroeter † includes under the same species the forms on *Cystopteris fragilis* and *Phegopteris Dryopteris,* recognizing, it seems, no essential differences for the forms on the two hosts. He describes the species in language resembling that of Winter, but with the exception that he mentions two kinds of uredospores respectively distinguished by thin and thick walls. It is suggested that perhaps the thick-walled spores are teleutospores. Dietel,‡ after examining some American and European collections, principally herbarium material, concludes that the differences in size of spores and the position of the sorus on the frond between the form on *Phegopteris Dryopteris* and the form on *Cystopteris fragilis* and other genera are sufficient to separate them. He would therefore refer the form on *Phegopteris Dryopteris* to *Uredo Aspidiotus* Pk.,* which is distinguished by having the sori on both sides of the leaf, but more abundant on the upper side; the spores are more or less polygonal or oval, measuring 36–56 × 27–40 μ, with from six to eight germ pores irregularly distributed over the surface. Dietel also emphasizes the constant appearance of thin-walled and thick-walled spores in both *Uredo Aspidiotus* Pk. and *U. Polypodii* (Pers.) DC. He mentions finding intermediate stages between the thin and the thick-walled spores, which seem to show that the one is developed from the other; but he entertains doubts as to which might be the primary form. Bearing in mind the suggestion of Winter as to the possibility of a teleutosporic form, he made cultures of the thick-walled type, yet the germination was that of true uredospores. It was then concluded that there were two kinds of uredospores in each of these species. It was also found that the thin-walled spores possess the constant character of four germ pores equatorially arranged, but this will be discussed later.

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* Rabenhorst, Kryptogamenflora, Pilze I. Abth. I. p. 253.

† Kryptogamenflora von Schlesien.

‡ Ueber *Uredo Polypodii* (Pers.), Oesterreichische Botanische Zeitschrift, XLIV., No. 2, February, 1894.

As far as I can ascertain, no views have been advanced as to the definite relationship of the thick-walled and thin-walled spores in regard to the relative time of development. For this purpose, as well as for a careful interpretation of specific distinctions, fresh specimens are essential. For the present study I was fortunate to secure from Arlington, Mass., fresh material of *Uredo Polypodii* (Pers.) DC. on *Cystopteris fragilis*; and at Shelburne, N. H., I found a supply of the form on *Phegopteris Dryopteris* described as *Uredo Aspidiotus* Pk. Access to an abundance of herbarium material, to be mentioned later, left no doubt as to the correct identification of the above named specimens. These two forms were carefully examined and compared in the fresh condition. In the form on *Cystopteris fragilis* the sori appear only on the under side of the leaf, and the spores are often smaller than in the case of the form on *Phegopteris Dryopteris*, but with these exceptions the general characters are the same. In either case, sections across the youngest sori show the thin-walled spores attached, and no thick-walled spores are present. The thin-walled spores are irregularly elliptical or oval (Figures 1, 2, 5, and 6), with very little trace of the orange contents. The whole number of germ pores is difficult to ascertain. In optical section one germ pore is often visible on each side about half-way between the apex and base, but more than one germ pore to a side is not infrequent, even in those spores possessing the thinnest walls. As I have stated, thick-walled spores are rarely to be seen in the young sori; but they are more abundant with the increasing age of the sorus, and the best defined of this type are always found unattached. These spores have orange-colored contents in the fresh condition. They are more or less oval in outline, with from four to eight germ pores generally indefinitely distributed over the surface, as in Figures 4, 8, and 10, taken from dried material. In every sorus showing both kinds of spores it needed little search to find connecting stages of every grade between the irregularly elliptical thin-walled spores and the oval or polygonal thick-walled spores. The cell wall is found in different degrees of thickness, and the number of well defined germ pores manifestly increases in proportion to this thickness of wall. Then from these results we derive the necessary conclusion that the thin-walled spores are merely the immature condition of the thick-walled mature uredo form.

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* Twenty-fourth Report of N. Y. State Museum, p. 88.

The herbarium material utilized in this study represented a number of host-plants, and the collections were made in widely separated localities; the diversity of material, therefore, should give a broad basis for reaching definite results. I have examined *Uredo Aspidiotus* Pk. on *Phegopteris Dryopteris*, Myc. Univ. 950, the material from the author of that species; also *Uredo Polypodii* (Pers.) DC. on the same host from Krieger, Fung. Sax. 566, Syd. Ured. 746, and a specimen collected by Dr. Farlow at Shelburne, N. H. I have studied specimens on *Cystopteris fragilis* bearing names as follows: *Uredo Polypodii* (Pers.) DC., Krieger, Fung. Sax. 567, and *Uredo Filicum* Desm., Erbario Critt. Italiano, 889; also material from Switzerland collected by P. Magnus and by Winter, and from Granville, Mass., Manitou, Col., Oregon, Gorham, N. H., and from near Boston, Mass. Other herbarium material included a specimen on *Phegopteris Dryopteris* from Thumen, Franconia, Germany; and *Uredo Polypodii* (Pers.) DC. on *Polypodium Dryopteris*, Eriksson, Fung. Paras. Scand.. 70 b. I must admit that with the examination of only a few preparations of herbarium material I might be inclined to agree with previous writers in distinguishing two distinct kinds of uredospores, but the fresh material showed beyond doubt that the two forms are but different phases in the development. Likewise, this process of development was traced in all of the herbarium specimens above enumerated. Figures 1 to 8 inclusive show two series in which this development may be traced.

In view of Dietel's mention of the four germ pores equatorially disposed in the thin-walled spores, it was thought well to study this further; hence young sori were isolated, the spores cleared and stained.

The disposition of the germ pores thus made clearer is various, and I failed to find any constant number relative to any special zone. Figures 11, 12, 13, and 14 are examples seen. At most, a study of the germ pores of spores in such immature condition is unsatisfactory on account of the slight differentiation of the walls.

We may now proceed to a more detailed consideration of what may be the specific distinctions or likenesses in all of the specimens examined. It has been seen that the general characters of the mature spores are the same, the number and distribution of the germ pores varies within certain definite limits, and the process of development shows the same peculiarity — if one may term it such — of thin-walled and thick-walled spores. It remains for a comparison of measurements to lend weight one way or another. As Dietel's results would indicate, the form on *Cystopteris fragilis* is smaller than that on *Phegopteris Dryopteris*, but this did not prove entirely constant, nor is the average difference great. The following are the full limits of the spore measurements on the different genera: *Phegopteris Dryopteris*, Krieg. Fung. Sax. 566, 30–52 × 17–35 μ; Eriksson. Fung. Paras. Scand. 70 *b*, 24–40 × 16–35 μ; *Phegopteris Dryopteris*, from Germany, 26–40 × 18–24 μ; *Cystopteris fragilis*, 20–40 × 16–27 μ. One specimen on *Cystopteris fragilis* from Massachusetts measured 20–30 × 16–21 μ, while another specimen on the same host and from the same State gave 24–40 × 23–27 μ; thus the extremes on the same host showed a variation quite as marked as that characterizing the forms on different hosts. From these results it seems conclusive that these forms should all be referred to the same species, *Uredo Polypodii* (Pers.) DC.

The specimens on *Cystopteris fragilis* and *Polypodium Dryopteris* often show a slight roughness on the outer wall, and this character was more clearly seen in fresh specimens of the former. A *Uredo* on *Adiantum Capillus-Veneris* from Cavara, Fung. Longobardiæ, and one on *Woodsia glabella* from New Hampshire, have this roughened appearance; but the general characters of the spores seem undoubtedly those of *Uredo Polypodii* (Pers.) DC. The limited material hardly justifies a positive assertion. A Californian form on *Pteris aquilina* is distinctly echinulate, but in the general form and size of the spores it agrees with others studied. If it belongs to the same species at all, it is certainly an extreme form.* Fresh specimens are necessary for accurate demonstration.

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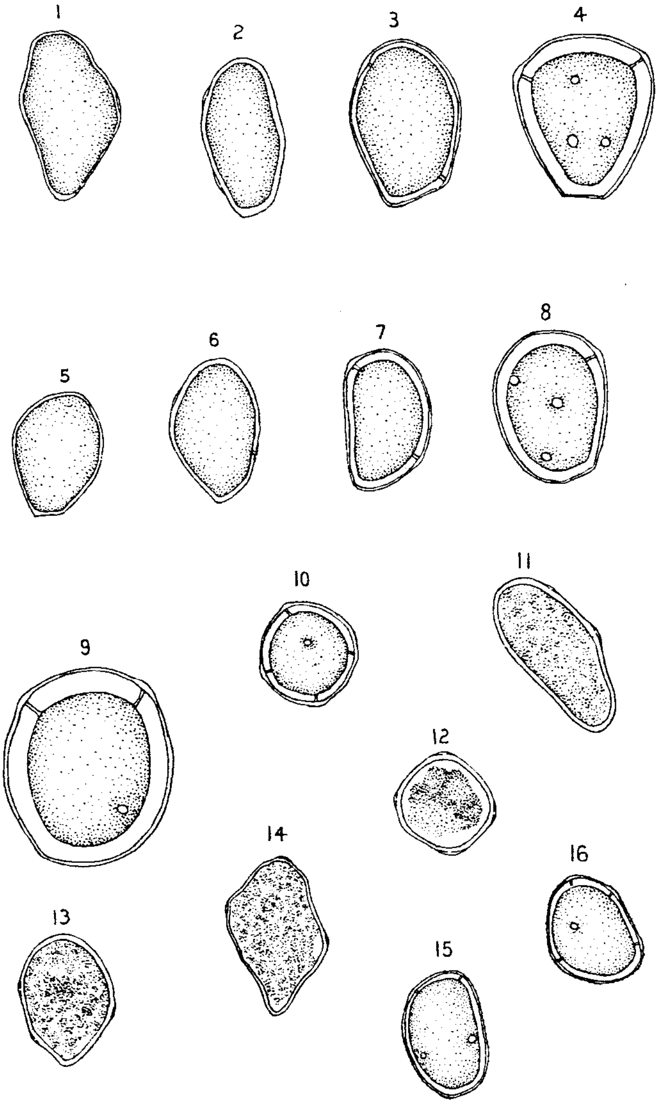
* Since the above notes were prepared for publication Dietel has described in Erythea, Vol. II. No. 8, [August, 1894,] *Uredo Pteridis* D. & H., on *Pteris aquilina*; and from his description it is plainly the form to which I have referred.

EXPLANATION OF THE PLATE.

All figures were drawn with the aid of an Abbé camera, using a Leitz objective No. 7 and ocular No. 3, reduced one fourth.

Figs. 1–4. Stages in the development of the form on *Phegopteris Dryopteris*, from Shelburne, N. H.
" 5–8. Similar stages as seen on *Cystopteris fragilis*, from Manitou, Col.
" 9, 10. Extreme sizes noted on *Phegopteris Dryopteris*, Eriksson, Fung. Paras. Scand. 70 *b*.
" 11–14. Immature spores on *Phegopteris Dryopteris*, cleared and stained, showing position of germ pores.
" 15. A spore of the form on *Woodsia glabella*.
" 16. From specimen on *Adiantum Capillus-Veneris*.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B.M.D. del.

Duggar on Uredo Polypodii.

XVII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

TRINITROPHENYLMALONIC ESTER.

By C. Loring Jackson and C. A. Soch.

Presented May 9, 1894.

At the end of his paper on the action of sodium acetacetic ester on picrylchloride, Dittrich* states that, in spite of many and varied attempts, he had not succeeded in making a picrylmalonic ester from picrylchloride and sodium malonic ester, but that he obtained in every case sodic picrate and viscous products of the decomposition of the malonic ester. This statement impressed us as a strange one, since in work † done in this Laboratory it had been found that tribromdinitrobenzol acted much more easily with sodium malonic ester than with sodium acetacetic ester; for whereas a good yield of the substituted malonic ester could be obtained even when the reaction took place in the cold, with the acetacetic ester the yield was small even after the reagents had been boiled together. Accordingly, we took up the study of this subject, and found, as we had expected, that the picrylmalonic ester could be obtained without difficulty. It is a white substance melting at 59°, and forms a blood-red sodium salt, which is tolerably stable, dissolving in water without decomposition. The picrylbrommalonic ester $C_6H_2(NO_2)_3CBr(COOC_2H_5)_2$ was made by treating the substituted malonic ester with an excess of bromine; it melts at 85°–86°. One object in undertaking this work was to see whether any trinitrobenzol was formed in the action of sodium malonic ester or sodium acetacetic ester on picrylchloride by the replacement of the atom of chlorine by hydrogen after the analogy of such reductions, which have been noticed frequently in the work done in this Laboratory upon tribromdinitrobenzol and tribromtrinitrobenzol. Unfortunately the research was begun so late in the year that we have been unable to arrive at a definite conclusion on this subject, and it is hoped that it will be possible to repeat the experiments on a larger scale and with conclusive results early in the coming term. A bromdinitrophenylbrommalonic ester corresponding to the picryl compound mentioned above was also prepared. It melts at 72°–73°.

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* Ber. d. ch. G., XXIII. 2720.

† These Proceedings, XXIV. 2, 274.

Trinitrophenylmalonic Ester (*Picrylmalonic Ester*), $C_6H_2(NO_2)_3CH(COOC_2H_5)_2$.

As Dittrich* states that the product of the reaction of picrylchloride and sodium malonic ester is viscous, we first turned our attention to the preparation of the sodium salt of the substituted malonic ester in the hope that this might be purified more easily than the free ester.

Sodium Picrylmalonic Ester, $C_6H_2(NO_2)_3CNa(COOC_2H_5)_2$.

The picrylchloride used in making this substance was prepared according to the method of Clemm,† except that we crystallized the chloride from a mixture of chloroform and alcohol, as we found that the addition of the chloroform made it possible to work with much smaller volumes of the solvent, and also seemed to prevent in great measure the deposition of the picrylchloride in an oily form. A strong cold benzol solution of 10 grams of this picrylchloride was mixed with an alcoholic solution of sodium malonic ester made from 14 grams of malonic ester and the sodic ethylate from 2.1 grams of metallic sodium. The mixture, which took on at once a deep red color, was cooled at first, and then allowed to stand for twelve hours at ordinary temperatures; after which it was diluted with about three quarters of a litre of water. In this way a red aqueous solution was obtained, and a supernatant layer of benzol which contained a portion of the picrylmalonic ester formed, while the rest was dissolved as a sodium salt in the red aqueous solution, in addition to some sodic picrate and the sodic chloride. Upon acidifying the aqueous liquid with sulphuric acid a yellow precipitate was thrown down, which as it settled from the liquid collected in an oily state on the bottom of the beaker. To the oily product a strong solution of sodic hydrate was added, which imparted to it a dark red color, and after thorough mixing converted it into a red crystalline solid. To remove any liquid or viscous impurities from the salt, it was next dissolved in the smallest possible amount of alcohol and treated with an excess of benzol, after which the mixed solutions were evaporated cautiously on the steam bath until crystals began to form, when upon cooling the sodium salt was obtained in fine red crystals; these were washed with benzol, and after drying in a desiccator gave the following results on analysis: —

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* Ber. d. ch. G., XXIII. 2720.

† Journ. Prakt. Chem., [2.], I. 145.

I. 0.2400 gram of the substance after evaporation with sulphuric acid gave 0.0427 gram of sodic sulphate.

II. 0.8331 gram of the substance gave 0.1429 gram of sodic sulphate.

	Calculated for $C_6H_2(NO_2)_3CNa(COOC_2H_5)_2$.	Found I.	Found II
Sodium	5.85	5.76	5.56

An additional quantity of the salt was obtained by the treatment just described from the residue left after evaporating off the benzol from the solution of picrylmalonic ester in this solvent obtained by adding water to the product of the reaction.

Properties of the Sodium Salt of Picrylmalonic Ester. — It crystallizes from a mixture of alcohol and benzol in dark red crystals often a centimeter long. It is easily soluble in alcohol or ether; somewhat less soluble in water than in alcohol; nearly insoluble in benzol. It does not seem to be decomposed by any of these solvents. Strong sulphuric acid decomposes it, but without any explosion, which surprised us, as it showed a tendency to explode when dry even at comparatively low temperatures.

As the potassium salt of picric acid is so much less soluble than the sodium salt, we prepared the potassium salt of the picrylmalonic ester by treating the free ester with potassic hydrate in strong aqueous solution; but, although this salt was somewhat less soluble in both water and alcohol than the sodium salt, the difference was not very marked, and there would be no advantage in using the potassium salt instead of the sodium salt in the purification of the substance.

The behavior of an aqueous solution of the sodium salt of picrylmalonic ester with various reagents was also studied, and the following more or less characteristic precipitates were obtained: —

Salt of magnesium, heavy reddish flocks.

Salts of calcium or barium, granular or crystalline precipitates of an amethyst color.

Salt of manganese, dirty yellow flocks.

Salt of nickel, light red flocks.

Salts of lead or silver, dark red flocks.

Salt of cadmium, reddish yellow flocks.

Picrylmalonic Ester, $C_6H_2(NO_2)_3CH(COOC_2H_5)_2$.

Although in our earlier experiments we prepared this substance through its sodium salt on account of the discouraging statements of Dittrich, we soon found that this was unnecessary, as the substance could be purified directly without difficulty, and in all our later work we have adopted this direct method, which we are about to describe, as it is much more convenient than the method of purification by means of the sodium salt. To prepare the picrylmalonic ester we proceeded according to the method described under Sodium Picrylmalonic Ester, until by the addition of water the product had been divided into an aqueous and a benzol solution. The aqueous solution after acidification with dilute sulphuric acid was allowed to stand until the oily precipitate had separated completely from the mass of the liquid; part of it settled, part floated on the surface, and even during this comparatively short standing the floating part was converted into crystals, which could be used to promote the crystallization of the larger quantity on the bottom of the beaker. This solidification of the main portion of the oily product was effected without difficulty by cooling with running water, one of the crystals from the surface of the water being added if necessary; and the solidified product, after washing with cold water, was crystallized from alcohol. The benzol solution, which had been separated from the aqueous solution, was acidified with dilute sulphuric acid, and allowed to evaporate spontaneously, when it furnished a rather large additional quantity of the oily product, which however, did not solidify so easily as that obtained from the aqueous portion, since it was necessary to allow it to stand for three or four days with occasional stirring in order to bring it into a crystalline condition. It was then pressed between layers of filter paper, which removed an oily impurity, after which it was mixed with the crystals obtained from the aqueous liquid, and the whole purified by crystallization from alcohol until it showed the constant melting point 59°, when it was dried in a desiccator, and analyzed with the following results: —

I. 0.2707 gram of the substance gave 28.6 c.c. of nitrogen at a temperature of 25° and a pressure of 757.4 mm.

II. 0.2565 gram gave 25.9 c.c. of nitrogen at a temperature of 22° and a pressure of 755.8 mm.

	Calculated for $C_6H_2(NO_2)_3CH(COOC_2H_5)_2$.	Found.	
		I.	II.
Nitrogen	11.32	11.75	11.38

It is worthy of remark that, whereas Dittrich from the action of picrylchloride on sodium acetacetic ester obtained a considerable quantity of dipicrylacetacetic ester, our principal product was the monopicrylmalonic ester, and only on one occasion have we observed a trace of a substance with a much higher melting point, which we took to be the dipicryl compound. We should add that, in applying the same method to the action of sodium acetacetic ester on picrylchloride, we obtained almost exclusively monopicrylacetacetic ester.

Properties of Picrylmalonic Ester. — It crystallizes from alcohol in white, long, rather slender rectangular plates, which develop into rather thick prisms with blunt ends often as much as two centimeters long. It melts at 59°, and is very soluble in chloroform, ether, benzol, or glacial acetic acid; somewhat less soluble in carbonic disulphide; soluble in cold alcohol, freely in hot; rather more soluble in methyl than in ethyl alcohol; insoluble in ligroine or cold water, slightly soluble in hot water. All the solutions of this substance except that in glacial acetic acid have a pink color, which is the more marked the stronger the solution, and the alcoholic solution imparts to the fingers a crimson color not unlike rosaniline, although less purple. This coloration of the fingers is much deeper than the color of the solution, and is tolerably fast. The formation of these pink or crimson colors from the white crystals is striking, and will be more carefully studied.

Cold strong sulphuric acid dissolves it; if this solution is warmed it turns red, and gives off bubbles of gas; dilution of the red solution after it had cooled precipitated a yellow solid. Strong nitric acid acted in the same way, except that the picrylmalonic ester dissolves more slowly in cold nitric acid than in sulphuric acid. Strong hydrochloric acid did not dissolve it in the cold, but on warming the substance melted, and then went into solution very slowly. The picrylmalonic ester has well marked acid properties forming the red sodium salt when treated with an aqueous solution of sodic hydrate. As is often the case with substances of this class, the sodium salt is nearly insoluble in a strong solution of sodic hydrate. The sodium salt is also formed by the action of a solution of sodic carbonate on the free ester.

Trinitrophenylbrommalonic Ester (Picrylbrommalonic Ester), $C_6H_2(NO_2)_3CBr(COOC_2H_5)_2$.

This substance was made by dissolving some of the trinitrophenylmalonic ester described in the preceding section in a small quantity of glacial acetic acid, and adding liquid bromine until it was present in distinct excess, as shown by the reddish brown color of the liquid. To make certain that the reaction was complete, the liquid was warmed gently on the steam bath for a few minutes, and then allowed to stand at ordinary temperatures for an hour, after which water was added in excess, giving a pale yellow precipitate partly solid and partly liquid. After this had settled, the supernatant liquid, colored red with the excess of bromine, was poured off, and the liquid part solidified by cooling. It was then washed with water, dried by pressure on filter paper, and purified by recrystallization from alcohol until it showed the constant melting point 85°–86°, when it was dried in a desiccator, and analyzed with the following result: —

0.1873 gram of the substance gave by the method of Carius 0.0789 gram of argentic bromide.

	Calculated for $C_6H_2(NO_2)_3CBr(COOC_2H_5)_2$.	Found.
Bromine	17.78	17.93

It is obvious that this atom of bromine, the presence of which is shown by the analysis, may have entered the molecule in one of two different places, either replacing the hydrogen of the malonic ester radical, as in the formula given above, or replacing one of the atoms of hydrogen attached to the benzol ring. It is easy to determine which position the bromine occupies, for, if it is attached to the malonic ester radical, the substance will have lost all its acid properties, since the acid hydrogen has been replaced by the atom of bromine. In the second case, where the bromine is attached to the benzol ring, on the other hand, the acid properties will not be interfered with, but on the contrary will be somewhat increased if the bromine atom has any effect whatever. Upon treating our new substance with a solution of sodic carbonate no change was observed, whereas the picrylmalonic ester is converted at once into its red salt by this reagent; as, therefore, this substance has no acid properties, it follows that the bromine has entered the malonic ester radical, and the formula given above is the correct one.

Properties of Picrylbrommalonic Ester. — It crystallizes from alcohol in white plates, nearly but not quite square, and much striated; these plates are arranged in irregular rather long rosettes. Less commonly it occurs in bladed or pennate forms. In general appearance it resembles acetanilid. It melts at 85°–86°, and is very soluble in chloroform or benzol; rather less soluble in ether, carbonic disulphide, or glacial acetic acid; soluble in cold alcohol, freely soluble in hot; rather more soluble in methyl than in ethyl alcohol; insoluble in cold ligroine, soluble in it when hot although with some difficulty; essentially insoluble in water, whether hot or cold. The best solvent for it is alcohol. Its alcoholic solution shows a faint pink color, similar to that given by picrylmalonic ester, but less marked. Strong sulphuric acid dissolves it in the cold with a yellow color; upon warming this solution it becomes brownish black, and bubbles of gas are given off. Strong hydrochloric acid seems to have no action on it even when hot. In cold strong nitric acid it is insoluble, but dissolves easily if the acid is hot, and boiling this solution for a short time produces no signs of decomposition. A strong solution of sodic hydrate did not act upon it in the cold, but, when heated with it, gave a red solution. The solution here was undoubtedly preceded by removal of the bromine. As has been stated already, sodic carbonate does not act on this substance.

Bromdinitrophenylbrommalonic Ester, $C_6H_2Br(NO_2)_2CBr(COOC_2H_5)_2$.

This substance was made by dissolving the bromdinitrophenylmalonic ester in glacial acetic acid and adding to the strong solution an excess of liquid bromine. The bromdinitrophenylmalonic ester was made from tribromdinitrobenzol melting at 192° and sodium malonic ester.[*] After an excess of bromine had been added, as shown by the color, the liquid was warmed gently on the water bath for a short time, and, if the color had disappeared, more bromine added. It was then, after it was cool, precipitated with water, and the substance obtained solidified by cooling, if necessary; after which it was purified by crystallization from alcohol, until it showed the constant melting point 72°–73°. It is not wise, however, to rely on the melting point as the only proof of purity, since the bromdinitrophenylmalonic ester from which it is formed melts at 75°–76°; we have therefore always tested our product also with a solution of sodic hydrate, which gives a red salt with the mother substance, but has no effect in the cold on the desired compound. After purification it was dried in a desiccator, and analyzed with the following results: —

I. 0.3196 gram of the substance gave by the method of Carius 0.2451 gram of argentic bromide.

II. 0.1997 gram of the substance gave 0.1550 gram of argentic bromide.

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[*] These Proceedings, XXIV. 2.

	Calculated for $C_6H_2Br(NO_2)_2CBr(COOC_2H_5)_2$	Found.	
		I.	II.
Bromine	33.05	32.64	33.02

The fact that this substance is not acted on by cold sodic hydrate proves that it contains the second atom of bromine attached to the malonic ester radical and not to the benzol ring.

Properties of Bromdinitrophenylbrommalonic Ester. — It crystallizes from alcohol in long white prisms terminated by a single plane at an acute angle and arranged in radiated groups; these crystals are sometimes a centimeter long. It melts at 72°–73°, and is very soluble in benzol, chloroform, acetone, carbonic disulphide, or glacial acetic acid; not freely soluble in cold alcohol, but easily in hot; more soluble in methyl than in ethyl alcohol; insoluble in cold ligroine, slightly soluble in hot; insoluble in water, but if boiled with water for some time, fresh water being added to take the place of that which evaporates, it is finally brought completely into solution. This action is undoubtedly due to the removal of the side-chain bromine as hydrobromic acid. It will be studied more carefully hereafter. Strong sulphuric acid does not act upon it in the cold, and when hot it acts only very slowly. Strong nitric acid also has no action when cold, but if hot dissolves it. Strong hydrochloric acid does not act upon it in the cold, and when hot has rather less effect than sulphuric acid. Strong solutions of sodic hydrate and ammonic hydrate have little or no action in the cold; when warmed they convert it into a red substance, probably a salt formed after the removal of the side-chain atom of bromine. The whole subject of the replacement of this second atom of bromine by other radicals must be studied more carefully before any account can be given of it. It is hoped that this work can be carried on in this Laboratory during the coming term.

XVIII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ACTION OF SODIC ALCOHOLATES ON CHLORANIL. ACETALS DERIVED FROM SUBSTITUTED QUINONES.*

By C. Loring Jackson and H. S. Grindley.

Presented May 9, 1894.

Introduction.

During the study of the action of sodic alcoholates, sodium malonic ester, and similar reagents upon tribromdinitrobenzol and related substances,† carried on now for some years in this Laboratory, it has been observed repeatedly that one of the atoms of bromine is replaced by hydrogen. In all this work, however, the bromine replaced by hydrogen has stood in the meta position to two other atoms of bromine, and, as it was possible that this strange reaction depended on the symmetrical position of the three atoms of bromine, we undertook the study of a substance with a different constitution; and for this purpose selected chloranil, in which no one of the atoms of halogen is in the meta position to two others. While this substance was well fitted for our work, because the atoms of chlorine which it contains can be replaced with comparative ease, on the other hand the action of most of these reagents with it had been already studied by Stieglitz,‡ Ikuta,§ Kehrmann,|| and others, and in no case could we find any mention of a direct replacement of chlorine by hydrogen; but still as it was

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* The work described in this paper formed a thesis presented to the Faculty of Arts and Sciences of Harvard University for the Degree of Doctor of Science, by H. S. Grindley.

† These Proceedings, XXIV. 1, 234, 256, 271, 288; XXV. 164; XXVII. 280; XXIX. 228.

‡ Am. Chem. Journ. XIII. 38.

§ These Proceedings, XXVI. 295.

|| Journ. Prakt. Chem., [2.], XL. 365.

possible that the compounds formed by such a replacement might have been overlooked among the secondary products of some of these reactions, or might be formed under other conditions, we have carried through our experiments. In fact, one of them has proved that, when sodic methylate acts upon chloranil, a reduction takes place, but the hydrogen, instead of replacing chlorine, reduces part of the chloranil to the corresponding tetrachlorhydroquinone. The work with chloranil, therefore, did not throw light on the replacement of bromine by hydrogen in tribromdinitrobenzol, because of the presence of the two atoms of quinone oxygen, which seized upon the hydrogen before it could replace the halogen. In the mean time, however, our experiments have led to interesting results of another sort, which are described in this paper.

The action of potassic phenylate on chloranil was the first selected for study, and we found that, if the substances were mixed in the proportion of two molecules of the former to one of the latter, the product was dichlordiphenoxyquinone, $C_6Cl_2(OC_6H_5)_2O_2$, which melts at 243°, and gives a hydroquinone melting at 197°–198° when treated with reducing agents. With the object of replacing the two remaining atoms of chlorine we next treated the dichlordiphenoxyquinone with aniline, but instead of acting on the atoms of chlorine this reagent attacked the phenoxy groups, giving dichlordianilidoquinone and phenol, behaving in this respect in the same way as dichlordimethoxyquinone, which, Kehrmann* found, was converted by treatment with aniline into dichlordianilidoquinone. This action we found was the normal one for our substance; for example, sodium malonic ester gave with the dichlordiphenoxyquinone the dichlorquinonedimalonic ester melting at 132° discovered by Stieglitz †; and, strangely enough, this indirect method of preparing the substance gives a better yield than the direct action of sodium malonic ester on chloranil, for while Stieglitz by this latter method obtained only about 10 per cent, our yield was as high as 27 per cent. The beautiful bright blue sodium salt $C_6Cl_2O_2[CNa(COOC_2H_5)_2]_2$ was obtained, and analyzed; it is stable for a malonic ester salt. The "deep pure violet color, resembling exactly a concentrated solution of potassium permanganate," obtained by Stieglitz upon the addition of sodic hydrate to the substance, is due, according to our observations, to some decomposition of the salt brought about by an excess of the alkali. The solution of the pure salt has the full blue color of aniline blue.

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* Journ. Prakt. Chem., [2.], XL. 370.

† Am. Chem. Journ., XIII. 38.

Sodic methylate acted on the dichlordiphenoxyquinone like the two reagents already mentioned; that is, the two phenoxy groups were replaced by two methoxy groups; but this action was followed by another and more interesting one, which formed a crystalline salt, appearing as a precipitate, if the amount of methylalcohol used as the solvent was small. Upon the addition of an acid to this salt a white substance was set free having the following formula:

$$C_6Cl_2(OCH_3)_2O_2(CH_3OH)_2.$$

The sodium salt was also analyzed, and proved to have the formula

$$C_6Cl_2(OCH_3)_2O_2(CH_3ONa)_2(CH_3OH)_2.$$

The two molecules of methyl alcohol appearing in this last formula are evidently only alcohol of crystallization, as they could be easily driven off by heat. The corresponding ethyl compound,

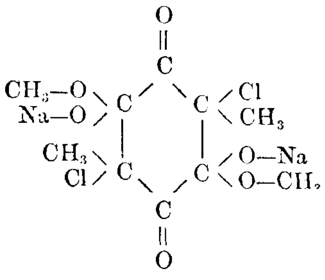
$$C_6Cl_2(OC_2H_5)_2O_2(C_2H_5OH)_2\,,$$

and the methylethyl compound,

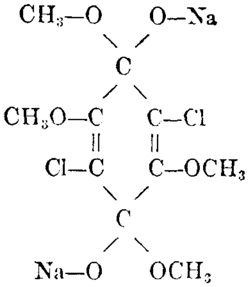
$$C_6Cl_2(OCH_3)_2O_2(C_2H_5OH)_2\,,$$

were also obtained, and resembled the methyl compound most closely in properties. In considering the way in which the two molecules of methyl alcohol (or sodic methylate) are attached to the molecule of $C_6Cl_2(OCH_3)_2O_2$, only two formulas seemed to us sufficiently probable to merit discussion. In the first of these (I.) the double bonds of the benzol ring are broken, and the radicals NaO and CH_3 added directly to the ring after the manner of the bromine and chlorine addition compounds discovered by Nef.* In the second (II.) the NaO and CH_3 have been added to the two carbonyl groups of the quinone, transforming it into a substance closely related to the acetals.

I.



II.



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* Am. Chem. Journ., XII. 483; XIII. 422.

The various isomeric forms of Formula I. need not be considered, as the arguments which follow will apply as well to them as to this one. From the properties of the substance, it is not possible to decide between these formulas. It is white, like Nef's bromine addition products, but an acetal like Formula II. would also probably be white, as the colors of chloranil and its derivatives undoubtedly depend on the fact that they are quinones, and in such an acetal as this the quinone nature is obliterated. Its most striking property is the ease with which the free substance loses the two additional molecules of methyl alcohol, since it passes into dichlordimethoxyquinone when heated to temperatures from 160° to 195°; the same change is brought about by dilute sulphuric or hydrochloric acid, slowly in the cold, more rapidly when the mixture is warmed gently. While this instability is in harmony with the second formula given above, it is hard to connect it with the first, as it seems improbable that a methyl group attached directly to the benzol ring, as in Formula I., could be so easily removed. It must be remembered in this connection, however, that Stieglitz* by treating the dichlorquinonedimalonic ester with dilute sodic hydrate in the cold obtained parachlorhydroxyquinone, $C_6ClOHH_2O_2$. As in this case carbon atoms attached to the quinone ring were removed by a dilute alkali in a few minutes, it might be that the methyl group in Formula I. could be removed under the conditions observed by us. The objection to Formula I. mentioned above might also be met by substituting for it one in which the radicals added were Na and CH_3O instead of NaO and CH_3 as in that formula, but such an addition seems to us at the best improbable. It should be remarked here that Nef's bromine addition compounds were decomposed with the utmost ease by alkalies, but were very stable in contact with acids, being crystallized from strong nitric acid; our substances show just the opposite behavior, as they are rather remarkably stable toward alkalies; but this difference might be due to the difference in the nature of the radicals added (Br_2 in one case, NaO and CH_3 in the other) rather than to a difference in the structure of the compounds.

Since, as explained above, the properties of our new substance were not sufficient to prove the correctness of one or the other of the two formulas proposed, we next turned our attention to some experiments with derivatives of this substance, or rather of the corresponding ethyl compound, which have settled the question conclusively.

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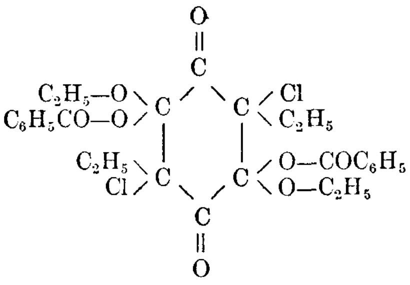
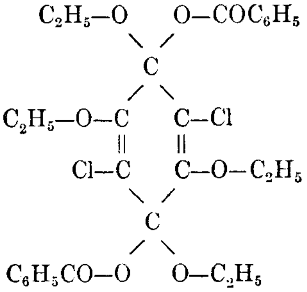
* Am. Chem. Journ., XIII. 38.

To obtain material for this work, which would be possessed of the requisite stability, we replaced the sodium in the salt of our substance with the benzoyl radical forming a compound which must have one of the following formulas, according as one or the other hypothesis about these substances is adopted.

I.



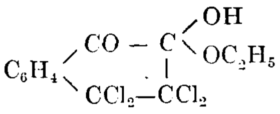
II.



In Formula I. the carbonyl groups are unaffected, and the body should therefore retain the properties of a diketone. In Formula II., on the other hand, the carbonyl groups having been transformed into acetal groups, the body should have lost its diketone nature. Accordingly, a substance constituted like Formula I. should be converted by reducing agents into a substance containing secondary hydroxyl groups, and by the chloride of hydroxylamine into a mono or dioxime. Upon treating our substance with zinc dust and glacial acetic acid, (which we have found the most efficient agent for converting quinones into hydroquinones,) it remained entirely unaltered, and the same result was obtained when we tried to act on it with chloride of hydroxylamine. The substance therefore shows neither of these characteristic reactions of the diketones and must be constituted according to Formula II. To meet the not overstrong objection that the diketone properties of the substance might have been weakened or destroyed by the presence of radicals attached to the ring, we treated dichlordiethoxyquinone with the reducing mixture, and also with chloride of hydroxylamine, and in both cases obtained a satisfactory quinone reaction. We tried also to determine the constitution of our substance in another way. This consisted in making the dichlordiethoxyquinone tetraethylacetal $C_6Cl_2(OC_2H_5)_2(OC_2H_5)_4$ by replacing the sodium in the sodium salt $C_6Cl_2(OC_2H_5)_2(ONa)_2(OC_2H_5)_2$ by ethyl, and then treating this dissolved in chloroform with bromine in the hope of making an addition product similar to those of Nef. The result of this experiment was negative, as no bromine was taken up, but this cannot be accepted as an argument against Formula II., since Nef[*] found that dichlordiethoxyquinone itself gives no addition compound with bromine, — a result which we can confirm. The failure of the tetraethylacetal to form addition compounds must be ascribed, therefore, to the presence of the two atoms of chlorine and two ethoxy groups attached to the quinone ring, rather than to the absence of double bonds.

It is perhaps worth noting that the formation of these hemiacetals is easily explained by the diketo formula of quinone, but cannot be brought into harmony with the peroxide formula, so far as we can find. Our work, therefore, would have been of value in determining the constitution of quinone, if it had been done before this question was finally settled by Nef's proof of the diketo constitution through his work on the action of bromine on argentic chloranilate.[†]

Since, as we have just proved, our new substance has the two molecules of methyl alcohol attached to the two carbonyl groups of the dichlordimethoxyquinone, it belongs to the class of acetals, and we propose to call it and similarly constituted bodies hemiacetals, because only half of the hydrogen in the hypothetical mother group of the acetals $=C=(OH)_2$ has been replaced by the organic radical. Such hemiacetals are not especially uncommon, the most familiar examples being the alcoholates of ordinary chloral and of butylchloral. Jacobsen,[‡] and later Renard,[§] claimed that they obtained the corresponding compound of acetaldehyd $CH_3CH(OH)(OC_2H_5)$, but do not agree in regard to its boiling point, and apparently assign to it a much greater stability than would be expected in such a substance. Without multiplying examples, we pass at once to some compounds more nearly related to ours, recently obtained by Zincke with some of his scholars. Zincke and Arnst [||] by the action of alcohol on tetrachlordiketohydronaphthalin have obtained a compound,



which is tolerably stable in the cold, but decomposed by heat, like our hemiacetal. The corresponding para compound formed no such derivative. Zincke and Neumann,* by the action of alcohol on nitro-β-naphthoquinone, obtained a substance the formula of which was made out as follows: —

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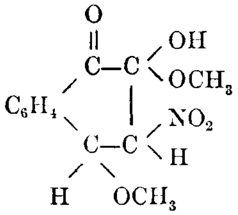
[*] Am. Chem. Journ., XI. 20, 24.

[†] Ibid., XII 466.

[‡] Ber. d. ch. G., IV. 215.

[§] Ber. d. ch. G., VIII. 132.

[||] Ann. Chem., CCLXVII. 319.



Still later, Zincke and Schaum † have made similar compounds from the isomeric heptachlorketotetrahydrobenzols by the action of sodic methylate. Although Zincke's work shows that ring ketones, orthodiketones, and orthoquinones are capable of forming such hemiacetals, so far as we can find our compound is the first of this class to be made from a paraquinone, and the compound of Zincke's which approaches most nearly to it, the orthoquinone derivative, differs from it strikingly, for, whereas in our compound both carbonyls are converted into hemiacetal groups, in Zincke and Neumann's only one of the carbonyl groups is thus affected, and at the same time a molecule of sodic methylate is added to the ring by the breaking of a double bond. It should be mentioned here that J. U. Nef ‡ has assumed the formation of addition products of water or hydrochloric acid with the carbonyls of quinone in explaining the formation of hydroquinone by the action of water,§ or substituted hydroquinones by the action of hydrochloric acid on quinone; ‖ but he supposes that these intermediate products break up immediately, and none of them have been isolated.

The discovery of the hemiacetals of the quinones has suggested to us a possible explanation of the constitution of quinhydrone and the bodies related to it. The most important of these substances are quinhydrone, formed from one molecule of quinone and one of hydroquinone; resorcinequinone, from one molecule of quinone and one of resorcine; phenoquinone, from one molecule of quinone and two of phenol; and quinhydronedimethylether, from one molecule of quinone and two of the monomethylether of hydroquinone. The state of our

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[*] Ann. Chem., CCLXXVIII. 173.

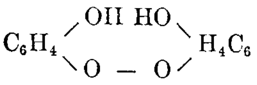
[†] Ber. d. ch. G., XXVII. 537.

[‡] Am. Chem. Journ., XIII. 427; Ann. Chem., CCLXX. 323; Clark, Am. Chem. Journ., XIV. 553.

[§] Hesse, Ann. Chem., CCXX. 367; Ciamician, Gazz. Chim., XVI. 111.

[‖] Levy, Schultz, Ann. Chem., CCX. 133; Sarauw, Ibid., CCIX. 93.

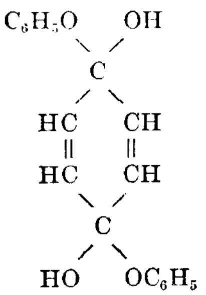
knowledge of the constitution of these substances is described in the following quotation from a paper on this subject by Nietzki:[*] "Aus vorstehenden Versuchen scheint hervorzugehen, dass das Chinhydron, das Chinonresorcin, blosse Additionsproducte des Chinons mit phenolartigen Körpern sind, und zwar scheint hierbei die Zahl der in letzteren enthaltenen freien Hydroxyle stets den beiden Chinonsauerstoffen zu entsprechen. Eine Formel im Sinne der Structurtheorie lässt sich für diese Körper wohl augenblicklich kaum aufstellen, denn die von Kekulé für das Chinhydron vorgeschlagene Structurformel

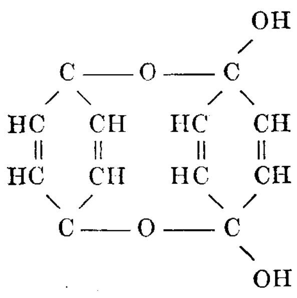


$$C_6H_4\begin{matrix}\diagup OH \quad HO \diagdown \\ \diagdown O \; - \; O \diagup\end{matrix}H_4C_6$$

lässt sich für die Verbindungen des Chinons mit einwerthigen Phenolen nicht mehr anwenden. Aus dem von O. Hesse beobachteten Verhalten des Chinhydrons gegen Essigsäureanhydrid scheint jedoch hervorzugehen dass das Chinhydron keine freien Hydroxyle enthält. Auch das von Wichelhaus beobachtete Verhalten des Monomethylhydrochinons spricht dafür, dass Substitutionsproducte des Chinhydrons in den Hydroxylgruppen nicht existiren."

It appears from this quotation that there is no satisfactory theory for the constitution of these compounds, since the statement that they are addition products amounts to saying that we have no theory on the subject. We would, therefore, advance the following theory in regard to the constitution of these bodies: that they are hemiacetals similar to those described in this paper; in phenoquinone the phenol, in quinhydrone the hydroquinone, taking the place of the methyl or ethyl alcohol, which is added to the substituted quinones in our new substances. On this theory the graphical formulas of phenoquinone and quinhydrone would be written as follows: —





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[*] Ann. Chem., CCXV. 136.

The principal arguments in favor of this theory are the following. It requires the union of one molecule of quinone with one molecule of a diatomic phenol such as hydroquinone or resorcine, but with two of a monatomic phenol like common phenol or monomethylhydroquinone, and is in this respect in accordance with the facts. Such substances would not be formed when the hydroxyl groups of the phenols had been converted into alkyloxyl groups, and dimethyl hydroquinone has no action on quinone. The products should be unstable, as we have found that the stability of our new hemiacetals depends on the number and strength of the negative radicals attached to the quinone ring, and in these cases, where there are no negative radicals, we should expect a very slight stability. As a matter of fact, these substances are not only decomposed by acids or alkalies, but quinhydrone even by solution in neutral solvents.* The action of acetic anhydride giving diacetylhydroquinone and quinone,† which is brought up by Nietzki as a proof of the absence of free hydroxyl, is really in accordance with our theory, as our dimethyl hemiacetal with acetic anhydride gave methyl acetate and the quinone from which the hemiacetal was derived. All these observed facts, therefore, are in harmony with our theory. Against it is the marked color of all this quinhydrone group, whereas our hemiacetals are colorless. This may be due, however, to the difference in the nature of the radicals attached to the carbonyl groups, our hemiacetals containing methyl or ethyl, the quinhydrone group aromatic radicals, which might well give more colored compounds. It may be remarked in this connection, that, while the methyl or ethyl ether of resorcine is colorless, the simple resorcine ether itself is reddish brown. An attempt will be made next year to find other parallel cases. Another objection to our theory is, that no salts have been obtained from phenoquinone, whereas the substance, according to our formula, contains two free hydroxyls. Wichelhaus, who states that he obtained no salts of it, adds that the substance turns blue when treated with alkalies; this may indicate the formation of a salt not yet isolated. We have attempted to test our theory by experiment in this direction, but so far with little result. By treating phenoquinone with sodic ethylate, not in excess, we obtained a green salt; but, as much phenol was found in the filtrate, we are inclined to consider this salt at present rather a product of the action of sodic ethylate on the quinone formed by the decomposition, than a salt of the phenoquinone itself. If this interpretation of the observation is true, it has no bearing on our theory, as it shows only that the phenoquinone is easily decomposed by alkalies, this decomposition taking place before it had time to form a salt. We then tried the action of sodic phenylate on quinone, as according to our theory this should act as well, or even better than free phenol, and we have succeeded in getting an action in this case, a strongly colored product being formed; but these experiments were undertaken so late in the year that we had no time to isolate this substance for study. We should add that in the action of potassic phenylate on chloranil, described at the beginning of the experimental part of this paper, there are strong indications of the formation of a diphenylhemiacetal, as the liquid took on a blue-black color in the cold, which upon heating changed to the red of the dichlordiphenoxyquinone. The isolation of this hemiacetal, if possible, will throw a great deal of light upon our theory of the nature of phenoquinone. All these lines of work will be taken up in this Laboratory during the next academic year, and we hope that by means of these experiments we shall succeed in testing thoroughly our theory that quinhydrone and phenoquinone are hemiacetals of quinone. The curious addition compounds of the nitranilines and quinones * will also be considered in this connection.

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* Clark, Am. Chem. Journ., XIV. 574.

† Hesse, Ann. Chem., CC. 248.

The dichlordimethoxyquinone dimethylhemiacetal

$$C_6Cl_2(OCH_3)_2(OH)_2(OCH_3)_2,$$

although most conveniently made from the dichlordiphenoxyquinone by the action of sodic methylate, can also be obtained by the action of the same reagent on dichlordimethoxyquinone, or even on chloranil. In this last case the first product is a green sodium salt, which by treatment with water yields the sodium salt of the hemiacetal and the tetrachlorhydroquinone, mentioned at the beginning of this paper. With sodic ethylate and chloranil we have not succeeded in obtaining the corresponding ethyl compound; it may be, however, that this result was due to not finding the proper conditions for the reaction.

The dichlordiethoxyquinone tetraethylacetal

$$C_6Cl_2(OC_2H_5)_2(OC_2H_5)_4,$$

alluded to in the discussion of the constitution of the hemiacetals, was made by the action of ethyliodide in the cold on the silver salt of the corresponding hemiacetal. The yield was exceedingly small, most of

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* Hebebrand, Ber. d. ch. G., XV. 1973; Niemayer, Ann. Chem., CCXXVIII. 332.

the hemiacetal dropping back to dichlordiethoxyquinone. Its properties were strangely unlike those of the corresponding hemiacetal, for whereas the dichlordiethoxyquinone hemiacetal was essentially insoluble in all solvents, the tetraethylacetal was so easily soluble in all the common solvents except water, that it was hard to crystallize it from any of them. The most striking property of the hemiacetal was its instability, since it gave up ethyl alcohol at temperatures from 140° to 143°, becoming converted into the dichlordiethoxyquinone (melting at 104°–105°); the tetraethylacetal, on the other hand, melts without decomposition at 101°–102°, and from 205° to 275° sublimes apparently unaltered. The hemiacetal is converted into dichlordiethoxyquinone when treated with acids, even more easily than by heat, dilute sulphuric or hydrochloric acid acting on it slowly even in the cold, rapidly when warmed. This is its most marked property; in fact, it is so susceptible to the action of acids that in our earlier preparations we obtained a considerable amount of dichlordiethoxyquinone by drying the hemiacetal at ordinary temperatures, when it had not been washed enough to remove the last traces of acid. In order to bring about a similar decomposition of the tetraethylacetal it is necessary to boil it with sulphuric acid of specific gravity 1.44. A more dilute acid does not act upon it, and even this rather strong sulphuric acid has no action in the cold. With alkalies the hemiacetal forms crystalline salts, which are comparatively stable, since they dissolve in water without decomposition, and can be kept in the dry state for a moderate length of time. The stability of the substance toward alkalies is in marked contrast to its behavior with acids, as it is necessary actually to boil it with sodic hydrate in order to convert it into chloranilic acid. The tetraethylacetal can of course form no salts, as it contains no hydroxyl. It is even more stable toward alkalies than the hemiacetal, as sodic hydrate even when boiling or mixed with alcohol does not decompose it. Finally the hemiacetal is amorphous, the acetal crystallizes finely, so that almost the only property which they have in common is their white color. The salts of the hemiacetals which are not derived from the alkalies are insoluble in water.

The dichlordiethoxyquinone dibenzoyldiethylacetal,

$$C_6Cl_2(OC_2H_5)_2(OC_2H_5)_2(OCOC_6H_5)_2,$$

also mentioned in the discussion of the constitution of the hemiacetals, was made by the action of benzoyl chloride on the sodium salt of the corresponding hemiacetal suspended in alcohol. In this case the yield is good, about 66 per cent of the theoretical, so that this substance is much more accessible than the tetraethylacetal; it crystallizes well, and melts at 170°. It is a curious fact that none of the benzoyl compound is formed, if the sodium or silver salt of the hemiacetal is suspended in ether instead of alcohol, and treated with benzoylchloride. In order to obtain this benzoyl compound, therefore, it is essential to use alcohol as the diluent. The reaction with ether is apparently the same as that which occurs when the free hemiacetal or its sodium salt is heated to 100° with benzoylchloride, the products in this case being dichlordiethoxyquinone and ethyl benzoate.

When the dichlordiethoxyquinone-dibenzoyldiethylacetal is heated with sulphuric acid of specific gravity 1.44 it is converted into a new substance, the analysis* of which gave numbers corresponding to the formula $C_6Cl_2(OC_2H_5)_2(OCOC_6H_5)_2O$. This body must be formed by the saponification of two ethoxy groups by the sulphuric acid, whereas we should have expected that the acid would have attacked rather the two benzoate groups. Our experiments have not as yet given us any means of determining which pair of ethoxy groups has been saponified. From the formula established by analysis we should infer that, after the two ethoxy groups had been converted by saponification into two hydroxyls, a molecule of water was eliminated, leaving the atom of oxygen spanning the benzol ring between two atoms of carbon in the para position to each other. Our substance, therefore, would have some analogy to cineol, if the constitution ascribed to it by Brühl † is correct. We realize fully, however, that such an unusual constitution as this should not be considered established without the most convincing proof, and, as at present we are unable to give this, we propose it only as that which accords best with the results of analysis and the method of preparation of the substance. We have made some attempts to prepare derivatives of this substance in order to throw light on its constitution, and have found that hydriodic acid converts it into a substance probably having the formula $C_6Cl_2OC_2H_5OH(OCOC_6H_5)_2$ and melting at 164°, but we have not yet studied this substance thoroughly enough to advance any theory in regard to its constitution. Aniline also forms one or more compounds with the saponification product, which we have not yet succeeded in bringing it into a state fit for analysis. We must content ourselves, therefore, at present with this preliminary statement of our experiments on this subject, the study of which will be continued in this laboratory during the next academic year.

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* As our first analytical results approached the numbers calculated for the dichlordiethoxyhydroquinone dibenzoate $C_6Cl_2(OC_2H_5)_2(OCOC_6H_5)_2$, we thought that perhaps we had in hand this substance mixed with an obstinately adhering impurity, and accordingly we made it from the substituted hydroquinone in order to compare it with our substance, but found that the two were not identical, since it melts at 215°, while the melting point of our new substance is 142°. The bad results from our first analyses we found afterward to be due to the difficulty in securing a complete combustion of our saponification product, and, after taking special precautions to insure this, numbers were obtained from very carefully purified preparations agreeing excellently with those for the formula given above.

† Ber. d. ch. G., XXI. 461. Compare also Ibid., XXVII. 810.

The methyl compounds $C_6Cl_2(OCH_3)_2(OCH_3)_2(OCOC_6H_5)_2$, melting at 193°, and $C_6Cl_2(OCH_3)_2(OCOC_6H_5)_2O$, melting at 205°–206°, which agree with the corresponding ethyl compounds in every respect, have also been prepared. In order to determine whether other acid radicals would act like benzoyl we treated the sodium salt of the diethyl hemiacetal with chlorocarbonic ester, and obtained the dichlordiethoxyquinone diethylacetaldicarbonic ester

$$C_6Cl_2(OC_2H_5)(OC_2H_5)_2(OCOOC_2H_5)_2,$$

which melts at 122°–123°. In view of our experiments with the benzoyl derivative, the saponification of this substance promises interesting results.

We have tried a number of experiments to determine the limits of the formation of hemiacetals from quinones; and have found that the dibromdiphenoxyquinone, melting point 266°–267°, made from bromanil, forms a hemiacetal, which seems to be as stable as the one made from chloranil. The chlordiphenoxyquinone, melting point 169°–170°, made from trichlorquinone, also forms a hemiacetal, but this is much less stable than that containing two atoms of chlorine. Even the dimethoxydiphenoxyquinone yielded a hemiacetal, but it was so unstable that it decomposed spontaneously almost as soon as it was formed. So that the stability of the hemiacetals seems to depend on the number and strength of the negative radicals attached to the benzol ring. It was not very probable, therefore, that a hemiacetal of quinone itself could be isolated, but yet we felt it was necessary to try the experiment; and this has established the fact that quinone is acted on by sodic ethylate, although the product — a green salt — has so far resisted our attempts to purify it for analysis. Work with it is especially hard because of its very slight stability; it takes fire spontaneously, if dried in the air at ordinary temperatures; and although, if dried first in hydrogen, it does not take fire on mere exposure to the air, it glows like tinder when heated to temperatures as low as 40°. After we had abandoned for the present the attempt to analyze the green salt, we succeeded in throwing some light on its composition by determining the proportion of quinone to sodic ethylate necessary to form it, as we found that each molecule of quinone takes up one molecule of sodic ethylate, but it must be left to future experiments to decide whether the product is really a hemiacetal.

In all the work so far described in this paper only two of the atoms of chlorine in chloranil have been replaced by other radicals; we found, however, that the other pair of atoms of chlorine could be replaced by phenoxy groups, if the dichlordiphenoxyquinone was treated with sodic phenylate, or if chloranil was acted on by four equivalents of sodic phenylate. The tetraphenoxyquinone thus formed melted at 229°–230°, and offered a rather striking resistance to the action of reducing agents, although zinc dust and glacial acetic acid converted it into tetraphenoxyhydroquinone, $C_6(OC_6H_5)_4OH$, melting point 219°–220°. Toward acids the tetraphenoxyquinone shows a marked stability, but by boiling with a strong solution of sodic hydrate it was converted into the diphenoxanilic acid, $C_6(OC_6H_5)_2(OH)_2O_2$, which melts at about 276°. Sodic methylate converts tetraphenoxyquinone into the dimethoxydiphenoxyquinone by replacing two of its phenoxy by methoxy groups; the substance melts at 171°. The corresponding diethoxydiphenoxyquinone, melting at 128°, was formed, instead of tetraphenoxyquinone, when chloranil was treated with sodic phenylate made from phenol and sodic ethylate in alcoholic solution. It is a noteworthy fact that bromanil acts differently with sodic phenylate made in this way, giving the dibromdiphenoxyquinone. One other case was observed of the substitution of all four of the chlorine atoms of chloranil. This was when the dichlorquinone dimalonic ester of Stieglitz was boiled with alcohol and sodic carbonate, as it was converted into diethoxyquinone dimalonic ester melting at 115°. It is certainly strange that such a rather weak reagent should remove these two atoms of chlorine, which in other cases have seemed very firmly attached to the molecule. In all the reactions just described it is to be observed that the chlorine atoms or phenoxy groups are replaced in pairs, and this fact also appears in much of the work with chloranil previous to ours. This replacement of the radicals two at a time can probably be connected with the para position of the two atoms of oxygen, which in this case serve to diminish the attraction of these radicals to the benzol ring, and thus make it possible to replace them, as in the case of tribromdinitrobenzol ($BrNO_2BrNO_2Br$), melting point 192°, where the loosening nitro groups are in the meta position, all three of the bromine atoms are replaced in many reactions.

EXPERIMENTAL PART.

Action of Potassic Phenylate on Chloranil.

In order to study this action, 25 grams of chloranil suspended in 50 c. c. of water were treated with an aqueous solution of potassic phenylate, made from 12 grams of potassic hydrate and 25 grams of phenol, which gave the proportion of two molecules of potassic phenylate to one of chloranil. To obtain a good result in this process it was necessary that the chloranil should not be in too large crystals; if, therefore, the specimen used was well crystallized, it was reduced to the hydroquinone with sulphurous acid, and then oxidized with nitric acid, which left it in a finely divided form easily attacked by the solution of potassic phenylate. The potassic phenylate was added in small portions at a time, and the first few drops imparted to the liquid a chrome-green color, which gradually changed to blue-black as more of the solution was added, until at last the whole became very dark blue or nearly black. In order to complete the reaction the mixture was heated on the steam bath for thirty minutes, which changed the color from black to red. In the cold there were no signs of the formation of this red substance, but it began to appear as soon as the mixture was warmed. The solution was filtered, and the dark red solid remaining on the filter, after washing thoroughly with water and alcohol, was purified by crystallization from hot benzol until it showed the constant melting point of 243°.

The analysis of the substance dried at 100° gave the following results: —

I. 0.2138 gram of the substance gave on combustion 0.4692 gram of carbonic dioxide and 0.0637 gram of water.

II. 0.1510 gram of the substance gave, according to the method of Carius, 0.1206 gram of argentic chloride.

	Calculated for $C_6Cl_2(OC_6H_5)_2O_2$.	Found. I.	II.
Carbon	59.83	59.85	
Hydrogen	2.77	3.32	
Chlorine	19.67		19.75

From these results it is evident that the substance is dichlordiphenoxyquinone. The yield is very good, 25 grams of chloranil giving as a rule 26 to 30 grams of the new substance, that is, about 80 per cent of the theoretical yield.

Properties of Dichlordiphenoxyquinone, $C_6Cl_2(C_6H_5O)_2O_2$. — The substance crystallizes from benzol in beautiful red needles arranged in rosettes. It melts at 243°, and is very slightly soluble in alcohol even when hot, less so when cold, insoluble in cold and boiling water, difficultly soluble in boiling benzol, and only very slightly soluble in the cold; it is sparingly soluble in cold chloroform, more easily in hot, slightly soluble in cold glacial acetic acid, but easily when the acid is boiling; in ether, ligroine, carbonic disulphide, or acetone, it is insoluble. The three strong acids have no visible effect on it, hot or cold. It is readily saponified by a solution of sodic hydrate, forming chloranilic acid. It is not affected by sulphurous acid at 100° under the ordinary pressure, but is easily reduced to the corresponding hydroquinone by warming with hydriodic acid, or by the action of glacial acetic acid and zinc dust.

Dichlordiphenoxyhydroquinone, $C_6Cl_2(C_6H_5O)_2(OH)_2$.

This substance was prepared by mixing dichlordiphenoxyquinone with hydriodic acid (boiling between 123° and 126°), and heating for some time on the steam bath. The product formed by this reduction was purified by crystallization from boiling dilute alcohol (50 per cent) until it showed the constant melting point of 197°. The analysis of the substance dried at 100° gave the following results: —

I. 0.2147 gram of the substance gave on combustion 0.4678 gram of carbonic dioxide and 0.0723 gram of water.

II. 0.1578 gram of the substance gave by the method of Carius 0.1244 gram of argentic chloride.

	Calculated for $C_6Cl_2(OC_6H_5)_2(OH)_2$.	Found.	
		I.	II.
Carbon	59.51	59.41	
Hydrogen	3.31	3.73	
Chlorine	19.56		19.49

The change from the quinone to the hydroquinone is quantitative.

Properties of Dichlordiphenoxyhydroquinone. — It crystallizes from dilute alcohol (50 per cent) in large colorless prisms, or in little needles very much branched, forming thick arborescent masses which melt at 197°–198°, and are readily soluble in ethyl alcohol, methyl alcohol, or acetone; soluble in carbonic disulphide or hot glacial acetic acid; slightly soluble in chloroform, cold glacial acetic acid, or ether. It is insoluble in water, either cold or hot, benzol, or ligroine. Dilute or strong sulphuric acid or hydrochloric acid does not act on the dichlordiphenoxydroquinone even when hot. It dissolves in alkalies and is reprecipitated from the solution by acids. On long standing or boiling with sodic hydrate it is saponified, giving the sodium salt of chloranilic acid which separates in long dark carmine red needles.

By the action of oxidizing agents, such as ferric chloride, dilute nitric acid, or potassic dichromate in acid solution, it is easily changed to the corresponding quinone.

Action of Aniline on Dichlordiphenoxyquinone.

The dichlordiphenoxyquinone was treated with aniline in the expectation of removing the two remaining atoms of chlorine. For this purpose 1 gram of dichlordiphenoxyquinone was mixed with 5 grams of aniline, and the mixture warmed on the water bath for a few minutes. When cool, the large excess of aniline was removed by dilute sulphuric acid, and, after thorough washing, the dark-colored residue was purified by dissolving it in aniline, and then adding a small quantity of alcohol; in this way well formed dark brown crystals were obtained, melting at 287°–290°, and therefore probably the dichlordianilidoquinone, the melting point of which is given as 285°–290°. This substance was first prepared and studied by O. Hesse,* later by Knapp and Schultz.† To confirm this inference the crystals were dried at 100° and the chlorine determined.

0.1480 gram of the substance gave by the method of Carius 0.1174 gram of argentic chloride.

	Calculated for $C_6Cl_2(C_6H_5NH)_2O_2$	Found.
Chlorine	19.70	19.61

The reaction therefore took an unexpected course, since the anilido groups replaced the two phenoxy radicals instead of the two atoms of chlorine.

Action of Sodium Malonic Ester on Dichlordiphenoxyquinone.

It has been shown in the preceding section that aniline removes the phenoxy groups instead of the atoms of chlorine from dichlordiphenoxyquinone. We therefore next turned our attention to the action of sodium malonic ester upon it to see whether this reagent behaved in the same way. In order to study this reaction 1 gram of dichlordiphenoxyquinone suspended in 10 c.c. of absolute alcohol was treated with a little more than two equivalents of sodium malonic ester, which was made by treating 0.15 gram of metallic sodium with about 10 c.c. of absolute alcohol, and then adding 2 grams of malonic ester. On adding the sodium malonic ester, the solution turned very dark blue, and on standing a dark blue precipitate separated, which was filtered off and washed with alcohol, in which it is only slightly soluble. The precipitate dissolved readily in water with a beautiful blue color, and on the addition of an acid a slightly yellow crystalline product separated, which was purified by recrystallization from boiling dilute alcohol until it gave the constant melting point 132°. After drying at 100°, it gave the following results on analysis: —

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* Ann. Chem., CXIV. 306.

† Ibid., CCX. 187.

I. 0.2180 gram of the substance gave on combustion 0.3880 gram of carbonic dioxide and 0.0994 gram of water.

II. 0.1654 gram of the substance gave 0.0964 gram of argentic chloride.

	Calculated for $C_6Cl_2[CH(COOC_2H_5)_2]_2O_2$.	Found. I	II.
Carbon	48.68	48.53	
Hydrogen	4.46	5.06	
Chlorine	14.41		14.41

These results prove that the substance is dichlorquinonedimalonic ester. Four grams of the dichlordiphenoxyquinone gave a yield of about 1.5 grams of the malonic ester compound, that is, 27 per cent of the theoretical yield.

It is evident that this body must be formed through the replacement of the two phenoxy groups by two malonic ester radicals, and in fact it was not hard to detect the phenol, which formed the secondary product of the reaction. For this purpose the alcoholic filtrate from the sodium salt of the malonic ester derivative, after evaporation nearly to dryness, was diluted with water, and treated with a dilute acid, when the smell of phenol was very evident, and bromine water gave a voluminous white precipitate. This easy replacement of the phenoxy groups by the malonic ester radicals, even although the former are attached to a benzol ring, suggests other work in the same line, which will be undertaken in this Laboratory.

This dichlorquinonedimalonic ester crystallizes from dilute alcohol in long slender radiating needles of a yellow color, which melt at 132°, and are insoluble in cold or boiling water, soluble in cold or warm alcohol. It is not affected by weak oxidizing agents, but hydriodic acid reduces it to a white crystalline substance, which melts at

159°–160°, the melting point of the dichlorhydroquinonedimalonic ester discovered by J. Stieglitz;* our dichlorquinonedimalonic ester is therefore identical with that obtained by him from the direct action of sodium malonic ester on chloranil. Our indirect method of preparing it, however, gives a better yield than the direct method, 27 per cent instead of 10 per cent. That we might not intrude on this field of research already occupied by Stieglitz, we have confined our work on this substance to that necessary for establishing its identity.

Sodium Salt of Dichlorquinonedimalonic Ester,
$C_6Cl_2(CNa(COOC_2H_5)_2)_2O_2$.

In order to prepare this salt the dichlorquinonedimalonic ester was dissolved in ether, and treated with rather less than the required amount of sodic ethylate in a strong alcoholic solution. The sodium salt separated at once as a blue precipitate, which was repeatedly washed with ether by decantation, and dried over sulphuric acid and paraffine until the weight remained constant, after which the sodium was determined with the following result: —

0.2788 gram of the salt gave 0.0731 gram of sodic sulphate.

	Calculated for $C_6Cl_2(CNa(COOC_2H_5)_2)_2O_2$.	Found.
Sodium	8.57	8.49

The sodium salt has a beautiful blue color, and is very easily soluble in water, giving a solution of a blue color as intense and striking as that of aniline blue. It is somewhat soluble in alcohol, but insoluble in ether.

Diethoxyquinonedimalonic Ester, $C_6(OC_2H_5)_2(CH(COOC_2H_5)_2)_2O_2$.

In the first attempt to form the sodium salt of the dichlorquinonedimalonic ester, the substance was dissolved in absolute alcohol and boiled with an excess of dry sodic carbonate. When the sodic carbonate was first added, the alcoholic solution was colored dark blue; but after filtering out the excess of sodic carbonate and evaporating rapidly, the solution became nearly colorless, and left after the alcohol had been driven off a residue of almost white crystals, which were purified by crystallization from alcohol until the melting point remained constant at 115°. The analysis of the substance dried over sulphuric acid and paraffine gave the following results: —

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* Am. Chem. Journ., XIII. 38.

0.2010 gram of the substance gave on combustion 0.4122 gram of carbonic dioxide and 0.1242 gram of water.

	Calculated for $C_6(OC_2H_5)_2[CH(COOC_2H_5)_2]_2O_2$	Found.
Carbon	56.25	55.93
Hydrogen	6.25	6.86

It gave no test for chlorine. These results prove that the substance is diethoxyquinonedimalonic ester, and it is certainly strange that this substance should have been formed from the corresponding dichlor compound by the action of sodic carbonate and alcohol, in view of the fact that these two atoms of chlorine in other cases have proved hard to replace. The substance crystallizes in beautiful yellowish white needles melting at 115°, which are insoluble in water, readily soluble in alcohol or ether.

Action of Sodic Methylate on Dichlordiphenoxyquinone.—Dichlordimethoxyquinone Dimethylhemiacetal, $C_6Cl_2(OCH_3)_2(OH)_2(OCH_3)_2$.

In order to see whether the phenoxy groups in dichlordiphenoxyquinone would be removed by sodic methylate, as they were when it was treated with sodium malonic ester or aniline, 10 grams of the dichlordiphenoxyquinone were mixed with a methyl alcohol solution of a little less than four equivalents of sodic methylate, made by treating 2.5 grams of metallic sodium with 60 c.c. of methyl alcohol. The solution was warmed gently on the water bath, and stirred constantly; soon a white crystalline substance began to separate, and the red color of the dichlordiphenoxyquinone disappeared entirely. The solution was filtered, the residue washed with a little alcohol, dissolved in water, filtered again, and then treated with dilute sulphuric acid in excess, which set free a white insoluble compound. The properties of this substance indicated at once that the reaction had not consisted in a simple replacement of the phenoxy by methoxy groups, as in that case the product must have been the dichlordimethoxyquinone discovered by Kehrmann,* which is red, melts at 141°–142°, and is not insoluble in the common solvents. To prepare our new body for analysis it was filtered off, washed with water, alcohol, and then with water again; after which it was dissolved in dilute sodic hydrate, filtered, precipitated with dilute sulphuric acid, and washed thoroughly as described above. This treatment was repeated two or three times, until the substance was perfectly white and did not change color when washed with alcohol and ether, and then dried for a short time over sulphuric acid and paraffine. It was then analyzed with the following results: —

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* Journ. Prakt. Chem., [2.], XL. 370.

I. 0.2410 gram of the substance gave on combustion 0.3459 gram of carbonic dioxide and 0.1064 gram of water.

II. 0.2005 gram of the substance gave on combustion 0.2943 gram of carbonic dioxide and 0.9720 gram of water.

III. 0.1920 gram of the substance gave by the method of Carius 0.1851 gram of argentic chloride.

IV. 0.2372 gram of the substance gave by the method of Carius 0.2233 gram of argentic chloride.

	Calculated for	Found.			
	$C_6Cl_2(OCH_3)_2O_2(CH_3OH)_2$.	I.	II.	III.	IV.
Carbon	39.87	39.13	40.02		
Hydrogen	4.65	4.90			
Chlorine	23.59			23.83	23.28

These results indicate that the substance is a dimethoxydichlorquinone, to which two molecules of methyl alcohol have been added. To confirm this view of its composition the sodium salt was prepared and analyzed as follows. An excess of the insoluble compound was added to a solution of sodic methylate in a large quantity of methyl alcohol. As the sodium salt formed is soluble in methyl alcohol,* while the original compound is not, it was easy by filtering to obtain a pure solution of the salt, from which it was then precipitated by adding an excess of ether. The precipitate was repeatedly washed with ether by decantation, transferred to a weighed platinum crucible, dried over sulphuric acid and paraffine, and analyzed with the following results: —

I. 0.2372 gram of the salt gave 0.0828 gram of sodic sulphate.

II. 0.2887 gram of the salt gave 0 1025 gram of sodic sulphate.

	Calculated for	Found.	
	$C_6Cl_2(OCH_3)_2O_2(CH_3ONa)_2(CH_3OH)_2$.	I.	II.
Sodium	11.24	11.31	11.50

As these analyses indicate that the salt contains two molecules of methyl alcohol of crystallization, an attempt was next made to determine the amount of volatile matter which it contained, with the following result: —

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* In the preparation of the original substance the sodium salt was obtained as a precipitate, because the amount of methyl alcohol used was not enough to dissolve it.

0.3177 gram of the salt heated at 100° lost 0.0501 gram.

	Calculated for $C_6Cl_2(OCH_3)_2O_2(CH_3ONa)_2(CH_3OH)_2$.	Found.
Methyl Alcohol	15.64	15.77

Another sample of the sodium salt was then dried at 100° to a constant weight, and a sodium determination was made in the dry substance.

0.2422 gram of the salt gave 0.1018 gram of sodic sulphate.

	Calculated for $C_6Cl_2(OCH_3)_2O_2(CH_3ONa)_2$.	Found.
Sodium	13.33	13.61

These results show that, by the action of sodic methylate upon the dichlordiphenoxyquinone in the first place the two phenoxy groups are replaced by two methoxy groups, and then two molecules of sodic methylate are added directly to the molecule of dichlordimethoxyquinone formed by the first part of the action. The proof that these two molecules of sodic methylate are attached to the carbonyl groups of the quinone has been given in the introduction to this paper, and the new substance therefore is dichlordimethoxyquinone dimethylhemiacetal.

Other Methods of Preparing the Dichlordimethoxyquinone Dimethylhemiacetal.

This body can be made also directly from chloranil by the action of sodic methylate. When one equivalent of chloranil was treated with five or six equivalents of sodic methylate dissolved in methyl alcohol, a green salt containing sodium separated. This salt was dissolved in water rendered alkaline by a little sodic hydrate, and the addition of a dilute acid to this solution produced a dirty white precipitate, a portion of which was soluble in alcohol, while the rest remained undissolved. The insoluble part, after purification by dissolving in sodic hydrate and filtering, was precipitated again with dilute sulphuric acid, and washed with water and alcohol, after which it was dried in a desiccator, and the chlorine determined: —

0.2060 gram of the substance gave by the method of Carius 0.1962 gram of argentic chloride.

	Calculated for $C_5Cl_2(OCH_3)_2O_2(CH_3OH)_2$.	Found.
Chlorine	23.59	23.55

That this product was the same as that prepared from the dichlordiphenoxyquinone was shown also by its properties, which agreed with those observed for that substance, especially by its very characteristic reaction with dilute acids.

The other product obtained from the green salt formed by the action of sodic methylate on chloranil was dissolved in the alcohol used in washing the dirty white precipitate from dilute sulphuric acid; after evaporating off the alcohol, it was purified by recrystallization from dilute alcohol, and analyzed with the following result: —

0.2094 gram of the substance gave by the method of Carius 0.4841 gram of argentic chloride.

	Calculated for $C_6Cl_4(OH)_2$.	Found.
Chlorine	57.25	57.16

As it melts at 235°, there can be no doubt that it is the tetrachlorhydroquinone, the melting point of which is given by Sutkowski [*] as 232°. We are unable to determine at present whether this tetrachlorhydroquinone is due to a secondary reaction, or whether it proceeds from that by which the hemiacetal is made. Sodic ethylate does not act in this way with chloranil.

The dichlordimethoxyquinone dimethylhemiacetal is also formed when dichlordimethoxyquinone melting at 141°–142° is treated with two equivalents of sodic methylate dissolved in methyl alcohol.

Properties of the Dichlordimethoxyquinone Dimethylhemiacetal. — It is a white amorphous solid, insoluble in all the common solvents. It is very easily converted into the red dichlordimethoxyquinone, melting at 141°–142°, discovered by Kehrmann.[†] This change can be effected by heat alone, since in the neighborhood of 160° it begins to take on a slight reddish color, which becomes darker very slowly at this temperature, but when heated to 195° or higher the substance melts to a red liquid, at the same time increasing very much in volume and giving off many bubbles of gas consisting probably of the vapor of methyl alcohol. The decompostion point is not a definite one, as in different trials this action took place at temperatures sometimes as much as twenty or twenty-five degrees apart. An easier way to bring about this change is by treating the hemiacetal with dilute sulphuric acid or dilute hydrochloric acid, to either of which it shows itself remarkably susceptible, the decomposition taking place quantitatively, slowly in the cold, but quickly on warming. The ease with which it is attacked by dilute acids is its most striking property. Continued boiling with water or with dilute alcohol or glacial acetic acid brings about the same decomposition, as does also treatment of either the free substance or its sodium salt with benzoylchloride in a sealed tube at 100°, methyl benzoate being the secondary product. Acetic anhydride decomposes it in the same way, but more slowly; on the other hand, neither methyl nor ethyl iodide acts on the sodium salt or the free substance. The formation of the benzoic ester of the substance is described below.

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[*] Ber. d. ch. G., XIX. 2316.

[†] Journ. Prakt. Chem., [2.], XL. 370.

The hemiacetal is a weak acid, forming with sodic methylate the white crystalline sodium salt, the method of preparation and analyses of which have been given above. This salt is soluble in water or alcohol, insoluble in ether. With argentic nitrate a white non-crystalline silver salt is formed, which is insoluble in water, and easily decomposed.

Action of Sodic Ethylate on Dichlordiphenoxyquinone. — *Dichlordiethoxyquinone Diethylhemiacetal,* $C_6Cl_2(OC_2H_5)_2(OH)_2(OC_2H_5)_2$.

In order to study this action 10 grams of dichlordiphenoxyquinone were treated with an alcoholic solution of little less than four equivalents of sodic ethylate, which was made by treating 2.5 grams of metallic sodium with 60 c.c. of absolute alcohol. When the sodic ethylate was first added there was no apparent action, but on standing, even in the cold, the red color of the dichlordiphenoxyquinone gradually disappeared, and a white crystalline sodium salt was formed. After warming gently on the water bath to finish the reaction, the solution was filtered, the salt washed with alcohol, dissolved in water, filtered again, and then dilute sulphuric acid added in excess, which gave a bulky white precipitate. This was filtered off, washed with water, alcohol, and then with water again. In order to purify the substance further, it was dissolved in dilute sodic hydrate, filtered, precipitated again with dilute sulphuric acid, and washed thoroughly, as above. This treatment was repeated until finally the substance was perfectly white, and did not change color when washed with alcohol and ether, and then dried for a short time over sulphuric acid and paraffine. The product was analyzed with the following results: —

I. 0.2205 gram of the substance gave on combustion 0.3802 gram of carbonic dioxide and 0.1304 gram of water.

II. 0.2017 gram of the substance gave by the method of Carius 0.1614 gram of argentic chloride.

	Calculated for $C_6Cl_2(OC_2H_5)_2O_2(C_2H_5OH)_2$.	Found. I.	 II.
Carbon	47.06	47.02	
Hydrogen	6.16	6.57	
Chlorine	19.89		19.78

These results show that the action of the sodic ethylate on the dichlordiphenoxyquinone is analogous to that of sodic methylate. since two phenoxy groups are replaced by two ethoxy groups, and then two molecules of sodic ethylate are added directly to one molecule of the dichlordiethoxyquinone thus formed, giving the sodium salt of dichlordiethoxyquinone diethylhemiacetal. The yield of the sodium salt from 10 grams of dichlordiphenoxyquinone was usually a little less than 10 grams, and therefore, as the change from the sodium salt to the hemiacetal is nearly quantitative, we obtained over 75 per cent of the theoretical yield.

Properties of the Dichlordiethoxyquinone Diethylhemiacetal. — It is a white amorphous solid, which dissolves slightly in alcohol, but is partially decomposed by this solvent, so that it cannot be recrystallized from it. It is essentially insoluble in all the other common solvents. By boiling with dilute sulphuric or hydrochloric acid it is decomposed, and the same reaction takes place more slowly when it stands with the dilute acid in the cold. The product of the action in either case is a light red body melting at 104°–105°, after being purified by crystallization from alcohol, which is, therefore, dichlordiethoxyquinone, as this is the melting point ascribed to this substance by Kehrmann.* Stenhouse,† who discovered it, gives its melting point as 107° ; but even by repeated recrystallization we have not been able to raise the melting point above 104°–105°, and therefore have come to the conclusion that Stenhouse's higher number must be due to an error. The white insoluble hemiacetal melts at 140°–143°, or rather decomposes at this temperature, changing into the red dichlordiethoxyquinone, which then melts. From these properties it appears that the relationship between the diethyl and dimethylhemiacetals is of the closest sort.

Like the corresponding methyl compound the dichlordiethoxyquinone diethylhemiacetal has acid properties forming with sodic hydrate a sodium salt. It shows toward sodic hydrate a stability in marked contrast to its susceptibility to the action of dilute acids. as it is necessary to boil it with a strong solution of sodic hydrate in order to saponify it to chloranilic acid. The sodium salt of the diethylhemiacetal is white and crystalline, readily soluble in water, slightly soluble in alcohol, and insoluble in ether. The dried salt is slowly decomposed on standing in a closed bottle for several weeks, alcohol is given off, and a solid product left, which contains some sodic chloranilate and another body, or more than one, which we have not yet identified. The silver salt is insoluble, and has a slight brownish yellow color. It is blackened by light alcohol being set free. On warming with water a red substance is formed, probably chloranilic acid. Insoluble salts were also obtained with solutions containing barium, calcium, lead, or zinc, but they were not studied. The details of the preparation of the sodium and silver salts will be found under the preparation of dichlordiethoxyquinone tetraethylacetal later in this paper.

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* Journ. Prakt. Chem., [2], XL. 365.

† Ann. Chem., Suppl. VIII. 14.

Dichlordimethoxyquinone Diethylhemiacetal,

$C_6Cl_2(OCH_3)_2(OH)_2(OC_2H_5)_2$.

This substance was made by treating 0.9 gram of dichlordimethoxyquinone with an alcoholic solution of sodic ethylate made from 0.2 gram of metallic sodium and absolute alcohol. After warming the mixture for a few minutes, all the red dichlordimethoxyquinone disappeared, and a crystalline sodium salt was deposited. The liquid was then cooled, the precipitate filtered out, washed with a little alcohol, and dissolved in water, in which it is completely and easily soluble. The aqueous liquid after filtration was treated with dilute sulphuric acid, which threw down a white bulky precipitate of the free hemiacetal, and this, after thorough washing with water, alcohol, and ether, was dried over sulphuric acid and paraffine, and analyzed with the following result: —

0.1892 gram of the substance gave by the method of Carius 0.1627 gram of argentic chloride.

	Calculated for $C_6Cl_2\,OCH_3)_2(OH)_2(OC_2H_5)_2$.	Found.
Chlorine	21.58	21.26

The dichlordimethoxyquinone diethylhemiacetal, like those hemiacetals which have been described already, is an amorphous white solid, essentially insoluble in all the common solvents. It is decomposed at temperatures between 140° and 160°, forming a red substance, probably dichlordimethoxyquinone, and it is easily saponified by dilute acids.

Dichlordiethoxyquinone Tetraethylacetal, $C_6Cl_2(OC_2H_5)_2(OC_2H_5)_4$.

It has been stated already that ethyl or methyliodide did not act either on the free hemiacetal or its sodium salt; if, however, the silver salt of dichlordiethoxyquinone diethylhemiacetal was treated with ethyliodide, the corresponding tetraethylacetal was formed. As this compound could be obtained only in very small quantities and with great difficulty, it was necessary to prepare the sodium and silver salts of the hemiacetal on a large scale, which was done as follows. 40 grams of dichlordiphenoxyquinone were mixed with the sodic ethylate made by treating 10 grams of metallic sodium with 150 c.c. of absolute alcohol, and in order to complete the reaction the mixture was warmed on the steam bath for a few minutes, and then allowed to stand at ordinary temperatures for four or five hours. The sodium salt of the dichlordiethoxyquinone diethylhemiacetal, which separated in large amount, was filtered off, and washed thoroughly, first with a mixture consisting of equal parts of alcohol and ether, and finally with ether alone. In this way 40 to 42 grams of the essentially pure sodium salt were obtained instead of the 44 grams required by the theory; the yield, therefore, was between 90 and 95 per cent of the theoretical.

In order to prepare the silver salt of the diethylhemiacetal, a concentrated aqueous solution of the sodium salt was treated with 25 grams of argentic nitrate dissolved in a small amount of water. The insoluble silver salt was filtered, washed thoroughly with water, alcohol, and ether, and then dried as quickly as possible by sucking a stream of air through it on the filter pump.

The silver salt of the dichlordiethoxyquinone diethylhemiacetal was then suspended in ether, and treated in the cold with ethyl iodide, when, in addition to a very small quantity of the tetraethylacetal, a large amount of dichlordiethoxyquinone was obtained. The acetal was separated from the quinone by treating the products of the reaction with a dilute solution of sodic hydrate in 50 per cent alcohol, which converted the dichlordiethoxyquinone into the sodium salt of chloranilic acid, while the dichlordiethoxyquinone tetraethylacetal was not affected by it. By washing with water it was then easy to separate the freely soluble sodic chloranilate from the insoluble acetal, which was purified by recrystallization from ligroine until it showed the constant melting point 101°–102°, when it was dried in a desiccator, and on analysis gave the following results: —

I. 0.2039 gram of the substance gave on combustion 0.3928 gram of carbonic dioxide and 0.1335 gram of water.

II. 0.2177 gram of the substance gave on combustion 0.4181 gram of carbonic dioxide. The water determination was lost.

III. 0.1843 gram of the substance gave by the method of Carius 0.1304 gram of argentic chloride.

IV. 0.1620 gram of the substance gave 0.1135 gram of argentic chloride.

	Calculated for	Found.			
	$C_6Cl_2(OC_2H_5)_2(OC_2H_5)_4$.	I.	II	III.	IV.
Carbon	52.30	52.54	52.37		
Hydrogen	7.26	7.28	—		
Chlorine	17.19			17.49	17.32

The yield, as has been already stated, is very small.

Properties of Dichlordiethoxyquinone Tetraethylacetal. — This substance can be obtained from ligroine in good-sized white rhombic prisms, but when more rapidly crystallized it forms irregularly fan-shaped groups of very much branched needles resembling certain delicate seaweeds, or four-sided plates nearly but not quite rectangular and much striated. It melts at 101°–102°. By heating in a capillary tube it is apparently not decomposed even at so high a temperature as 275°, but between 260° and 275° it sublimes, giving beautiful white crystals in the upper part of the tube. It is very easily soluble in ether, benzol, alcohol, chloroform, acetone, ligroine, glacial acetic acid, carbonic disulphide, acetic anhydride, or methyl alcohol, but is insoluble in water. Ligroine is the best solvent for it.

It is saponified by sulphuric acid of specific gravity 1.44, giving the dichlordiethoxyquinone melting at 104°–105°, and also a small quantity of chloranilic acid. In the cold the acid produces little or no effect on the acetal, but after warming on the steam bath for half an hour the saponification is complete. A more dilute acid seems to have no action upon it. Sodic hydrate, even when boiling or mixed with alcohol, does not decompose the acetal.

The differences between the properties of the tetraethylacetal and the diethylhemiacetal certainly are remarkable. The hemiacetal is entirely insoluble, while the acetal is exceedingly soluble in all the common solvents except water. The former is very unstable, being readily decomposed by even very dilute acids, while the latter is saponified only slowly by comparatively strong acids when heated with them. By heat also the hemiacetal is easily decomposed, whereas the acetal sublimes apparently unaltered at high temperatures.

The action of bromine on the tetraethylacetal might prove of great interest, as the formation of addition products from it similar to those obtained by J. U. Nef* from quinone would prove that the four ethoxy groups were attached to the carbonyl radicals of the quinone molecule, and thus settle the constitution of this whole class of compounds. The chances of the formation of such addition compounds were, however, small, as Nef has shown † that dichlordiethoxyquinone does not take up bromine, a result which we can confirm; nevertheless we felt that it would be unwise to neglect this experiment. Accordingly, 0.5 gram of bromine dissolved in chloroform was added to 0.5 gram of the acetal also dissolved in dry chloroform. Even the first drop of the bromine imparted a distinct yellowish red color to the solution, showing that no bromine addition compound had been formed. When all the bromine had been added, the solution was allowed to evaporate spontaneously, and, although the residue was colored slightly, it was found that the weight had not increased, and after one recrystallization from ligroine it gave the melting point of the unaltered acetal 101°-102°. In another experiment the chloroform solution was evaporated to dryness on the water bath, and the same results were obtained. Under no conditions that we have found could the acetal be induced to take up bromine. The negative outcome of these experiments cannot be used in deciding the constitution of the acetal, since its inability to take up bromine is more likely to be due to the presence of the two atoms of chlorine and two ethoxy groups attached to the benzol ring than to the occupation of the double bonds by the four additional ethoxy groups, since dichlordiethoxyquinone does not take up bromine, as has been already stated.

Dichlordiethoxyquinone Dibenzoyldiethylacetal, $C_6Cl_2(OC_2H_5)_2(OC_2H_5)_2(OCOC_6H_5)_2$.

When the diethylhemiacetal itself or its sodium salt was treated with benzoyl chloride at 100° in a sealed tube, no benzoyl compound was formed, but the main products were dichlordiethoxyquinone and ethylbenzoate. A similar result was obtained when the sodium or silver salt of the hemiacetal was suspended in ether, and then treated with benzoyl chloride. When, however, the sodium salt was suspended in alcohol instead of ether and benzoyl chloride added, the dibenzoyl derivative was readily formed, and only a trace of dichlordiethoxyquinone was produced. The following method was found to be the best for the preparation of this substance. To 10 grams of the sodium salt of the dichlordiethoxyquinone diethylhemiacetal suspended

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[*] Amer. Chem. Journ., XII. 483.

[†] Ibid., XI. 20.

in a small quantity of alcohol 7.6 grams of benzoyl chloride were added, which gave the proportion of two molecules of benzoyl chloride to one of the sodium salt. There was but little action in the cold, but when the mixture was warmed on the water bath the reaction took place readily, with the separation of sodic chloride. After cooling, the solution was filtered, and the solid remaining on the filter washed thoroughly with alcohol and water, and then crystallized from hot alcohol until it showed the constant melting point 170°. The analysis of the substance dried at 100° gave the following results: —

I. 0.2428 gram of the substance gave on combustion 0.5276 gram of carbonic dioxide and 0.1230 gram of water.

II. 0.2173 gram of the substance gave by the method of Carius 0.1112 gram of argentic chloride.

	Calculated for	Found.	
	$C_6Cl_2(OC_2H_5)_2(OC_2H_5OCOC_6H_5)_2$.	I.	II.
Carbon	59.47	59.27	
Hydrogen	5.31	5.63	
Chlorine	12.57		12.65

The yield of the dichlordiethoxyquinone-dibenzoyldiethylacetal from ten grams of the salt is seven and one half grams, or about 66 per cent of the theoretical yield.

Properties of Dichlordiethoxyquinone Dibenzoyldiethylacetal. — From alcohol it crystallizes in short thick prisms, or, when crystallized more rapidly, in rhombic crystals with a sharp terminal angle, often collected into curving radiated or bladed groups. It is white, and melts at 170°. It is easily soluble in chloroform, carbonic disulphide, ether, or benzol; also in hot ethyl or methyl alcohol, but only slightly soluble in either of these liquids when cold; soluble in warm glacial acetic acid; slightly soluble in hot ligroine; insoluble in water. Sulphuric acid of specific gravity 1.44 saponifies it, forming the compound described in the next section. Sodic hydrate solution, even if boiling or mixed with alcohol, does not decompose it.

The study of the action of reducing agents and of hydroxylamine on the dichlordiethoxyquinone dibenzoyldiethylacetal was of especial interest, because it threw so much light upon the constitution of this whole class of substances. If this body was a true acetal, these agents should have no action upon it; if, on the other hand, the ethoxy and benzoyl radicals were not attached to the two carbonyl groups of the quinone molecule, but to the four other atoms of carbon, the substance would be converted into a secondary alcohol by reducing agents, and into an oxime by hydroxylamine. The reducing agent selected was a mixture of zinc dust and glacial acetic acid, as this had proved rather the most effective for the conversion of a quinone into a hydroquinone, and there was little or no danger that it would saponify the compound. Even after long continued action there were no signs of reduction, but the unaltered dichlordiethoxyquinone dibenzoyldiethylacetal was recovered from the mixture. This experiment, therefore, goes to prove that the substance is an acetal, and this proof is strengthened by the fact that dichlordiethoxyquinone is converted into the corresponding hydroquinone quickly and easily by this reducing mixture.

To try the action of hydroxylamine 0.2 gram of the dichlordiethoxyquinone dibenzoyldiethylacetal dissolved in alcohol was mixed with an alcoholic solution of 0.5 gram of hydroxylamine chloride. The solution was boiled over the free flame for half an hour, and then after cooling treated with a large excess of water. The precipitate thus formed after one crystallization from alcohol melted at 170°, and was therefore the unchanged original substance. No other organic substance could be found in the precipitate, or in the aqueous filtrate. The experiment was repeated with an alkaline solution, and again with an acid solution, but in no case could any change in the original acetal be detected. To prove that the indifference of the acetal to the hydroxylamine was not due to the effect of the ethoxy radicals and chlorine atoms attached to its benzol ring, we next studied the action of the chloride of hydroxylamine on dichlordiethoxyquinone. For this purpose 0.5 gram of it were treated with the chloride of hydroxylamine in alcoholic solution, and the mixture warmed for sixteen hours on the water bath. Water precipitated a black substance crystallized in scales, which was thoroughly washed with water to remove all the hydroxylamine salt. It dissolved easily in sodic hydrate, and from this solution acids threw down a reddish gelatinous precipitate. It gave a good test for nitrogen by the potassium method. There can be no doubt, therefore, that the chloride of hydroxylamine acts on dichlordiethoxyquinone and consequently the indifference of our acetal to this reagent is not due to the presence of the radicals attached to the benzol ring, but is caused by the occupation of the two carbonyl groups by the ethoxy and benzoyl radicals. As we had accomplished our purpose when we had proved that the chloride of hydroxylamine acts on dichlordiethoxyquinone, we have not tried to study the product more carefully.

Saponification of Dichlordiethoxyquinone Dibenzoyldiethylacetal.

This substance was boiled with sulphuric acid of specific gravity 1.44 for half an hour in a flask with a return condenser; a certain amount of gas was given off, and the solid finally went into solution completely, but upon cooling crystals were deposited, the amount of which was increased by diluting the acid with water. This crystalline precipitate was filtered out, washed repeatedly with water to remove a little chloranilic acid which had been formed in the process, and the residue recrystallized from alcohol until it showed the constant melting point 142°, when it was dried for analysis. The analysis of this substance gave a great deal of trouble; by using a boat and a stream of oxygen according to the usual method we were unable to secure complete combustion, and therefore were forced to mix the compound with cupric oxide, and carry on the combustion in an old-fashioned closed tube. This accounts for the fact that our percentages of hydrogen are somewhat high.

I. 0.2119 gram of the substance gave on combustion 0.4558 gram of carbonic dioxide and 0.0845 gram of water.

II. 0.2062 gram gave 0.4452 gram of carbonic dioxide and 0.0869 gram of water.

III. 0.2020 gram gave 0.4344 gram of carbonic dioxide and 0.0830 gram of water.

IV. 0.2063 gram gave 0.4451 gram of carbonic dioxide and 0.0837 gram of water.

V. 0.1947 gram of the substance gave by the method of Carius 0.1136 gram of argentic chloride.

VI. 0.2212 gram gave 0.1290 gram of argentic chloride.

	Calculated for $C_6Cl_2(OC_2H_5)_2(OCOC_6H_5)_2O$.	Found.					
		I.	II.	III.	IV	V.	VI.
Carbon	58.65	58.66	58.88	58.64	58.84		
Hydrogen	4.07	4.43	4.67	4.56	4.51		
Chlorine	14.46					14.42	14.41

The formula calculated from these analytical results is so strange, that we were at first unwilling to accept it, and thought that perhaps we had the dibenzoate of dichlordiethoxyhydroquinone in our hands, the calculated percentages of hydrogen and chlorine for which agree fairly well with those found by us, whereas the calculated percentage of carbon is over two per cent higher. This difference we thought might be due to an obstinate impurity, and accordingly we prepared this dibenzoate from dichlordiethoxyhydroquinone, and found that it was entirely different from the saponification product, as it melts at 215° instead of 142°. The description of this substance is given later in the paper. The supposition that the substance might contain an obstinately adhering impurity was disposed of by frequent recrystallizations. The sample for Analysis I. was crystallized only three or four times, that for II. and III. ten times, that for IV. eight times. There was no difference in the melting points of these three samples, and, as the results given above show, no essential difference in their percentage composition. We must therefore accept the formula derived from these analyses, and the most probable hypothesis is that the atom of oxygen spans the benzol ring between two atoms of carbon in the para position, but we are unable to determine at present whether this atom of oxygen proceeded from the saponification of the ethoxy radicals of the acetal, and therefore lies between the two atoms of carbon to which the benzoate groups are attached, or from the two ethoxy groups of the chloranilic ester, and therefore spans the ring between two other atoms of carbon. This latter supposition seems to us the more probable, as it would give some explanation of the ease with which the ethyls are removed. We wished to confirm such an unusual hypothesis by studying the derivatives of this substance, but our work in this direction has not yet brought any conclusive evidence in regard to its constitution, and we therefore propose this theory only as the most probable one, leaving to future work the testing of its accuracy. It may be observed here that such a substance would be a natural product of the saponification of dichlordiethoxyquinone dibenzoyldiethylacetal as shown by the following reactions: —

$$\begin{aligned}
&C_6Cl_2(OC_2H_5)_2(OC_2H_5)_2(OCOC_6H_5)_2 + 2\,H_2SO_4 = \\
&C_6Cl_2(OC_2H_5)_2(OH)_2(OCOC_6H_5)_2 + 2\,C_2H_5HSO_4 = \\
&C_6Cl_2(OC_2H_5)_2O(OCOC_6H_5)_2 + H_2O + 2\,C_2H_5HSO_4.
\end{aligned}$$

We would call the substance, in accordance with its provisional formula, oxide of dichlordiethoxyhydroquinone dibenzoate, although it may be instead the oxide of dichlorquinone ethylbenzoylacetal.

Properties of the Oxide of Dichlordiethoxyhydroquinone Dibenzoate. — It crystallizes in white well developed six-sided prisms, often of considerable size, belonging either to the hexagonal or orthorhombic system. When crystallized more quickly, it forms rather loose rosettes of prisms terminated by several planes forming a very blunt end. It shows a strong tendency to separate from its solutions in the form of a varnish, this result being obtained, for instance, when the alcoholic solution is evaporated to dryness on the water bath. It melts at 142°, and is readily soluble in alcohol or chloroform; soluble in carbonic disulphide, glacial acetic acid, or benzol; difficultly soluble in ether; insoluble in water. The best solvent for it is alcohol. With aniline it gives two or more products, the study of which next year we hope may throw some light on its constitution.

Reduction of the Oxide of Dichlordiethoxyhydroquinone Dibenzoate.

When the substance described in the preceding paragraph is moistened with a concentrated solution of hydriodic acid, and heated on the water bath until dry, a reaction takes place, as shown by the separation of free iodine. In order to complete the action the moistening with hydriodic acid and warming was repeated, and the product thus obtained was purified by repeated recrystallization from a very small quantity of alcohol until it showed the constant melting point 164°, when it was dried at 100°, and analyzed with the following results: —

I. 0.2004 gram of the substance gave on combustion 0.4339 gram of carbonic dioxide and 0.0812 gram of water.
II. 0.2301 gram of substance gave 0.5001 gram of carbonic dioxide and 0.0825 gram of water.
III. 0.2274 gram of substance gave by the method of Carius 0.1462 gram of argentic chloride.
IV. 0.1998 gram gave 0.1276 gram of argentic chloride.
V. 0.1990 gram gave 0.1276 gram of argentic chloride.

	Calculated for $C_6Cl_2OC_2H_5OH(OCOC_6H_5)_2$.	Found.				
		I.	II.	III.	IV.	V.
Carbon	59.06	59.06	59.28			
Hydrogen	3.58	4.50	3.99			
Chlorine	15.89			15.90	15.79	15.85

These results agree best with those calculated for the formula given above, although it is not impossible that the substance may contain more hydrogen. It is obvious, however, that the formula of the substance cannot be considered as established, until the analytical data have been supported by experiments with some of its derivatives. We shall not at present indulge in any speculations on the constitution of this substance. It crystallizes usually in balls of indistinct little prisms, but occasionally slender short prisms terminated by a single plane at a very sharp angle were observed. Like its mother substance, it has a strong tendency to come down from its solutions in the form of a varnish. It melts at 164°, and is very soluble in alcohol, much more so than the oxide from which it was obtained; easily soluble in acetone, or glacial acetic acid; sparingly soluble in ether, benzol, or chloroform; insoluble in carbonic disulphide, or water. It shows weak acid properties, since it dissolves in a solution of sodic hydrate, and is reprecipitated by an acid. Aniline acts upon it, but we have not yet studied the products. Alcohol seems to be the best solvent for it. The study of this substance will be continued in this Laboratory next year, and we hope the results of this work will not only definitely establish its formula, but also throw much light on the constitution of the body we have called the oxide of dichlordiethoxyhydroquinone dibenzoate, from which it was obtained.

Dibenzoate of Dichlordiethoxyhydroquinone,
$C_6Cl_2(OC_2H_5)_2(OCOC_6H_5)_2$.

This substance, which was made in order to compare it with the oxide of dichlordiethoxyhydroquinone dibenzoate just described was prepared as follows. The sodium salt of the substituted hydroquinone was treated with a slight excess of benzoyl chloride, and the product boiled with water to decompose the benzoyl chloride which had not entered into the reaction. After filtering hot the residue was recrystallized from a mixture of alcohol and chloroform until it showed the constant melting point 215°, when it was dried at 100°, and analyzed with the following result: —

0.2000 gram of the substance gave by the method of Carius 0.1202 gram of argentic chloride.

	Calculated for $C_6Cl_2(OC_2H_5)_2(OCOC_6H_5)_2$.	Found.
Chlorine	14.95	14.86

Properties of the Dibenzoate of Dichlordiethoxyhydroquinone. — It crystallizes from a mixture of alcohol and chloroform in long white prisms terminated by two planes meeting at an obtuse angle: these prisms show a tendency to unite longitudinally. It melts at 215°, and is easily soluble in chloroform; soluble in boiling benzol; sparingly soluble in alcohol even when hot, or in glacial acetic acid; insoluble in ether, carbonic disulphide, ligroine, or water. The dilute acids do not act on it even when boiling, nor does strong hydrochloric acid or strong nitric acid produce any visible effect; strong sulphuric acid also does not act on it in the cold, but when hot dissolves it, forming a slightly dark-colored solution. Alkalies even in strong boiling solution do not decompose it.

Dichlordimethoxyquinone Dibenzoyldimethylacetal,

$C_6Cl_2(OCH_3)_2(OCH_3)_2(OCOC_6H_5)_2$.

This substance was made in the hope that its saponification might throw some additional light on the curious products obtained from the corresponding ethyl compound, and described in the preceding sections. For this purpose 17 grams of the sodium salt of dichlordimethoxyquinone dimethylhemiacetal were suspended in methyl alcohol, and 20 grams of benzoyl chloride added (this is a little more than the calculated amount), after warming for a short time to finish the reaction, the liquid was allowed to cool, the solid, which had separated, filtered out, and washed first with alcohol and afterward with water. The residue was purified by crystallization from a mixture of alcohol and chloroform until it showed the constant melting point 193°, when it was dried at 100°, and analyzed with the following result: —

0.2052 gram of the substance gave by the method of Carius 0.1163 gram of argentic chloride.

	Calculated for $C_6Cl_2(OCH_3)_2(OCH_3)_2(OCOC_6H_5)_2$.	Found.
Chlorine	13.95	14.02

The substance crystallizes from a mixture of alcohol and chloroform in several different forms, which however may be produced by the twinning of a single form in different ways. The simplest form observed consisted of rather long plates terminated by two planes at an obtuse angle to each other; these frequently appeared as broad blades in radiating groups, when less well developed. A second very common form was white thick plates, square or nearly so, which showed evidence of twinning, and finally mixed with these were sharp thick rhombic crystals looking like very acute scalenohedra, and showing a line of twinning along the diagonal between the two acute angles. Whether these were different habits of the same form, or indicated that the substance was not homogeneous, mattered little to us, as the saponification with sulphuric acid of specific gravity 1.44 gave a product which was evidently homogeneous, and this was the substance in which we were especially interested. The dichlordimethoxyquinone dibenzoyldimethylacetal is white, and melts at 193°. It is easily soluble in chloroform; soluble in benzol; sparingly soluble in alcohol, ether, glacial acetic acid, or carbonic disulphide; insoluble in water or ligroine. The best solvent for it is a mixture of alcohol and chloroform.

Saponification of Dichlordimethoxyquinone Dibenzoyldimethylacetal.

The substance was boiled with sulphuric acid of specific gravity 1.44, in the manner already described under the corresponding ethyl compound, and the phenomena observed in this case were exactly similar to those presented by the ethyl compound. The product of the reaction was purified by recrystallization from a mixture of chloroform and alcohol until it showed the constant melting point 205°–206°, when it was dried at 100°, and analyzed with the following result: —

0.2071 gram of the substance gave according to the method of Carius 0.1288 gram of argentic chloride.

	Calculated for $C_6Cl_2(OCH_3)_2(OCOC_6H_5)_2O$.	Found.
Chlorine	15.33	15.38

This product therefore corresponds to that obtained by the saponification of the ethyl compound, and this view of its nature is confirmed by the striking similarity between these two substances in crystalline form.

Properties of the Oxide of Dichlordimethoxyhydroquinone Dibenzoate. — It crystallizes from a mixture of alcohol and chloroform in white well formed rhombic prisms, shorter than they are broad, terminated by a very obtuse octahedron and a basal plane forming a very blunt end; the prisms are frequently rendered six-sided by the presence of two basal planes on the acute edges. It melts at 205°–206°, and is readily soluble in chloroform; soluble in glacial acetic acid, or benzol; slightly soluble in alcohol, acetone, or carbonic disulphide; very sparingly soluble in ether; insoluble in water. The best solvent for it is a mixture of alcohol and chloroform.

Dichlordiethoxyquinone Diethylacetaldicarbonic Ester,
$C_6Cl_2(OC_2H_5)_2(OC_2H_5)_2(OCOOC_2H_5)_2$.

After we had succeeded in replacing the sodium in the salts of the hemiacetals described in this paper with the benzoyl radical, it seemed of interest to see whether other acid chlorides would act in the same way, and we therefore tried the action of chlorocarbonic ester. Four grams of the sodium salt of dichlordiethoxyquinone diethylhemiacetal suspended in absolute alcohol were mixed with a slight excess of chlorocarbonic ester, and warmed on the steam bath for a few minutes in order to complete the reaction. The solution was filtered while still hot from the precipitate of sodic chloride, and the filtrate on cooling deposited well formed crystals of the new substance, which was purified by recrystallization from alcohol until it showed the constant melting point 122°–123°, when it was dried, and analyzed with the following result: —

0.1866 gram of the substance gave by the method of Carius 0.1075 gram of argentic chloride.

	Calculated for $C_6Cl_2(OC_2H_5)_2(OC_2H_5)_2(OCOOC_2H_5)_2$.	Found.
Chlorine	14.18	14.24

The substance crystallizes in white flat prisms, terminated usually by a single plane at a very sharp angle, which is occasionally modified by a second smaller plane. It melts at 122°–123°, and is readily soluble in alcohol, chloroform, benzol, or acetone; soluble in glacial acetic acid, or carbonic disulphide; slightly soluble in ether; insoluble in water. The best solvent for it is alcohol. In view of the results of the saponification of the corresponding benzoyl compound the decomposition of this substance with sulphuric acid of specific gravity 1.44 promises to be interesting. Unfortunately, it was prepared just before the vacation, so that this work must be postponed until the next college year.

Action of Potassic Phenylate on Dichlordiphenoxyquinone. — *Tetraphenoxyquinone,* $C_6(OC_6H_5)_4O_2$.

By treating 10 grams of pure dichlordiphenoxyquinone with a little more than two equivalents of potassic phenylate, made by dissolving 4 grams of potassic hydrate and 12 grams of phenol in 150 c.c. of water, tetraphenoxyquinone was formed. In order to complete the reaction it was necessary to boil the dichlordiphenoxyquinone with the potassic phenylate for twenty to thirty minutes. The product formed was then filtered off, and after washing thoroughly with water and alcohol was purified by crystallization from benzol until it gave the constant melting point of 229°–230°. After drying at 100°, the substance gave the following results on analysis: —

I. 0.2198 gram of the substance gave on combustion 0.6122 gram of carbonic dioxide and 0.0865 gram of water.

	Calculated for $C_6(OC_6H_5)_4O_2$.	Found.
Carbon	75.63	75.97
Hydrogen	4.20	4.37

This body can also be formed by the action of four equivalents of potassic phenylate in aqueous solution on chloranil, or by the action of sodic phenylate on the dichlordiphenoxyquinone suspended in benzol. In this latter case the sodic phenylate was prepared by dissolving phenol in a rather large volume of benzol, and then adding the required quantity of sodium, which disappeared completely after warming the solution on the steam bath for some time. Neither of these methods gives so good a result as the one described at the beginning of this section. On the other hand, the tetraphenoxyquinone is not formed when the dichlordiphenoxyquinone is treated with sodic phenylate, which has been made by the action of metallic sodium on absolute alcohol mixed with phenol, as in this case the principal product is diethoxydiphenoxyquinone.

Properties of Tetraphenoxyquinone. — It crystallizes from benzol in red prisms which, when well developed, have blunt ends formed by a number of planes or by a single plane at an oblique angle. When smaller they appear as long somewhat shuttle-shaped prisms, radiating from a common centre, but not forming circular groups. It melts at 229°–230°, and is soluble in hot chloroform, boiling acetic anhydride, or boiling benzol; slightly soluble in carbonic disulphide, or boiling glacial acetic acid; very sparingly in warm acetone; insoluble in water, alcohol, ether, or ligroine. The best solvent for it is boiling benzol.

The tetraphenoxyquinone is not easily attacked by reducing agents; sulphurous acid at ordinary temperatures, or in a sealed tube at 100°, has no action on it; hydriodic acid, or a mixture of stannous chloride and hydrochloric acid, reduces it, but the action is very slow; on the other hand, it is easily reduced by glacial acetic acid and zinc dust.

Saponification of Tetraphenoxyquinone.

Toward acid saponifying agents the tetraphenoxyquinone shows a remarkable stability. Sulphuric acid of specific gravity 1.44 has no effect whatever, even after long continued boiling, but hot strong sulphuric acid of specific gravity 1.83 dissolves it, giving a solution from which nothing is precipitated on adding water. This may be due to the formation of a sulphonic acid, but we have not as yet studied the reaction carefully.

A better result was obtained by boiling the tetraphenoxyquinone with a solution of sodic hydrate (one part in four) for about two hours, as it was then completely dissolved, giving a dark purple color to the solution, which on cooling deposited small black crystals of a sodium salt. The alkaline solution, when poured into an excess of dilute acid, gave a reddish yellow precipitate, which was filtered out, washed with water, and, after purification by recrystallization from alcohol, dried, and analyzed with the following result: —

0.2224 gram of the substance gave on combustion 0.5436 gram of carbonic dioxide and 0.0794 gram of water.

	Calculated for $C_6(OC_6H_5)_2(OH)_2O_2$.	Found.
Carbon	66.68	66.65
Hydrogen	3.70	3.97

The substance was therefore formed from the tetraphenoxyquinone by replacing two of the phenyl radicals by hydrogen, and is the diphenoxyanilic acid.

Properties of Diphenoxyanilic Acid, $C_6(OC_6H_5)_2(OH)_2O_2$. — It forms glistening rather thick plates, either square or in rectangular oblong forms, having a dark reddish brown color like that of ferric citrate; which the substance also resembles in lustre and general appearance. It melts at about 276°, but the melting point is not sharp, as it shows signs of softening even at 270°. If heated somewhat above its melting point, it puffs up filling the capillary tube with a dark liquid. It is soluble in glacial acetic acid; sparingly soluble in alcohol or hot chloroform; insoluble in ether, benzol, carbonic disulphide, or ligroine. It dissolves slightly in boiling water, imparting a pink color to the solution. It has distinct acid properties dissolving in sodic hydrate to form a black crystalline salt, which dissolves in water with a dark purple color. It is not acted on by acids dilute or strong, cold or hot.

Tetraphenoxyhydroquinone, $C_6(OC_6H_5)_4(OH)_2$.

This body was made by reducing the tetraphenoxyquinone with glacial acetic acid and zinc dust. Two grams of the tetraphenoxyquinone were warmed on the steam bath with these reagents until the red color of the original substance had completely disappeared; water was then added, and the precipitated hydroquinone purified by recrystallizing it from alcohol containing a little hydriodic acid to prevent oxidation. On analysis the following results were obtained: —

0.2015 gram of the substance gave on combustion 0.5558 gram of carbonic dioxide and 0.0862 gram of water,

	Calculated for $C_6(OC_6H_5)_4(OH)_2$.	Found.
Carbon	75.32	75.21
Hydrogen	4.60	4.75

Properties of the Tetraphenoxyhydroquinone. — It crystallizes from alcohol in white well developed rather thick rhombic plates, with a very acute angle, which sometimes show sharp notches in the two ends. When seen on the edge the plates seem to be monoclinic, and are often twinned on the basal plane. Larger crystals are apt to have the form of sharp spear-heads. At 210°, it shows signs of decomposition by beginning to turn red. This change of color increases as the temperature rises, until finally it melts at 219°–220° giving a light red liquid, which on cooling solidifies to a red body, probably the quinone. It is readily soluble in acetone; somewhat more sparingly soluble in ethyl alcohol, methyl alcohol, or chloroform; sparingly soluble in cold glacial acetic acid, more readily in hot; very sparingly soluble in benzol or ether. It is insoluble in water, carbonic disulphide, or ligroine. Alcohol is the best solvent for it.

Diethoxydiphenoxyquinone, $C_6(OC_2H_5)_2(OC_6H_5)_2O_2$.

This substance was obtained in some of our earlier attempts to make tetraphenoxyquinone by treating dichlordiphenoxyquinone with sodic phenylate dissolved in absolute alcohol, 10 grams of dichlordiphenoxyquinone were mixed with two equivalents of sodic phenylate made by treating 1.6 grams of sodium with about 20 c.c. of absolute alcohol and then adding 8 grams of phenol. On the addition of the sodic phenylate the dichlordiphenoxyquinone became dark-colored, and a very black tarry solution was obtained, which after standing for two hours was separated by filtration from the sodic chloride formed; water was then added to the filtrate, which precipitated an oily black liquid. In order to purify this liquid it was repeatedly washed with water by decantation, and then dissolved in alcohol, from which beautiful silky orange-yellow needles were obtained, and these were recrystallized from alcohol until they showed the constant melting point 128°, when after drying in a desiccator they gave the following results on analysis: —

0.2104 gram of the substance gave on combustion 0.5324 gram of carbonic dioxide and 0.1004 gram of water.

	Calculated for $C_6(OC_2H_5)_2(OC_6H_5)_2O_2$.	Found.
Carbon	69.47	69.01
Hydrogen	5.26	5.30

The yield is small. The diethoxydiphenoxyquinone crystallizes in long silky orange-yellow slender needles arranged in radiating groups. It melts at 128°, and is readily soluble in alcohol or chloroform; soluble in carbonic disulphide or benzol; sparingly soluble in ether or glacial acetic acid; insoluble in ligroine or water. The best solvent for it is alcohol.

Action of Sodic Methylate on Tetraphenoxyquinone. (Dimethoxydiphenoxyquinone, $C_6(OCH_3)_2(OC_6H_5)_2O_2$.)

When 5 grams of tetraphenoxyquinone were treated with a solution of six equivalents of sodic methylate in methyl alcohol, it dissolved to a colorless liquid, which on standing deposited a quantity of nearly white needles. These were filtered off, and after washing with a little methyl alcohol treated with water rendered alkaline by sodic hydrate, when a portion of the substance was dissolved, and a yellow crystalline body was left as an insoluble residue. This latter substance was purified by crystallization from a mixture of benzol and alcohol until it showed the constant melting point 171°, when it was dried at 100°, and analyzed with the following result: —

0.2043 gram of the substance gave on combustion 0.5068 gram of carbonic dioxide and 0.0862 gram of water.

	Calculated for $C_6(OCH_3)_2(OC_6H_5)_2O_2$.	Found.
Carbon	68.19	67.66
Hydrogen	4.55	4.69

The substance is therefore dimethoxydiphenoxyquinone formed by the replacement of two of the phenyl by methyl radicals.

Properties of Dimethoxydiphenoxyquinone. — It crystallizes from a mixture of alcohol and benzol in beautiful long golden-yellow needles, which under the microscope are seen to be slender prisms arranged in radiating groups. The terminations of these prisms consist of one principal plane, sometimes at a right angle, sometimes at an oblique angle to the sides; in this latter case, when the crystals are large enough, small modifying planes are also seen. It melts at 171°, and is readily soluble in chloroform; soluble in ethyl or methyl alcohol, benzol, or glacial acetic acid; sparingly soluble in ether or carbonic disulphide; insoluble in ligroine or water. It is reduced by zinc and glacial acetic acid to a colorless hydroquinone.

It dissolves apparently with decomposition in a dilute solution of sodic hydrate, and from this solution dilute sulphuric acid precipitates a non-crystalline body insoluble in water, but soluble in sodic hydrate with a fine purple color. We have not had time as yet to study this substance more carefully.

When the yellow dimethoxydiphenoxyquinone was mixed with a solution of sodic methylate in methyl alcohol, and the mixture stirred vigorously, the yellow solid disappeared, and a white crystalline sodium salt was precipitated. This precipitate dissolved in water without residue, and from the solution the addition of a dilute acid threw down a white amorphous solid, which decomposed almost immediately into a yellow substance probably dimethoxydiphenoxyquinone. These observations show that in this case a hemiacetal was formed, but a much less stable one than that obtained from the quinones containing chlorine. It seems, therefore, that the stability of the hemiacetals depends on the number and strength of the negative radicals attached to the quinone ring.

Action of Sodic Phenylate on Bromanil.

In order to study this action 2 grams of bromanil, prepared according to Stenhouse,* were treated with an alcoholic solution† of sodic phenylate made by acting on 0.3 gram of sodium with absolute alcohol and then adding 3 grams of phenol. The bromanil began to turn red as soon as the phenylate was added, but it was necessary to warm the mixture in order to make the reaction complete. After this the solution was filtered, and the solid remaining on the filter, after thorough washing with water and alcohol, was purified by crystallization from benzol until it showed the constant melting point 266°–267°, when it was dried at 100° and analyzed with the following result: —

0.1677 gram of the substance gave, according to the method of Carius, 0.1393 gram of argentic bromide.

	Calculated for $C_6Br_2(OC_6H_5)_2O_2$	Found.
Bromine	35.56	35.36

The substance is, therefore, dibromdiphenoxyquinone, and it is to be observed that bromanil behaves differently from chloranil with this alcoholic solution of sodic phenylate, for the latter lost all four of its atoms of chlorine, two being replaced by phenoxy and two by ethoxy groups. The bromanil, on the other hand, behaves with the alcoholic solution of sodic phenylate as chloranil does with an aqueous solution of this reagent, the action consisting in the replacement of two atoms of halogen by two phenoxy groups.

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* Ann. Chem., Suppl. VIII. 13.

† This experiment was tried early in our work, before we had found that an aqueous solution of the sodic phenylate acted better on chloranil than the same reagent dissolved in alcohol. If we were to repeat this preparation, therefore, we should use a solution in water instead of in alcohol.

Properties of Dibromdiphenoxyquinone. — It crystallizes from benzol in rather short orange-red needles with blunt points, melting at 266°–267°. It is very slightly soluble in alcohol even when hot; insoluble in ether or ligroine, or in water whether cold or hot; sparingly soluble in carbonic disulphide or boiling benzol, and only very slightly soluble in cold benzol; more soluble in chloroform; freely soluble in hot glacial acetic acid, slightly in cold. The three strong acids have no visible effect upon it. By the action of glacial acetic acid and zinc dust it is reduced to a colorless hydroquinone. It reacts easily with sodic methylate, ethylate, or phenylate, and also with sodium malonic ester, or aniline, but we have studied only its action with sodic methylate.

Dibromdimethoxyquinone Dimethylhemiacetal,
$C_6Br_2(OCH_3)_2(OH)_2(OCH_3)_2$.

This body was formed by treating 1.4 grams of dibromdiphenoxyquinone with a solution of rather less than four equivalents of sodic methylate in methyl alcohol, which was made by the action of a little methyl alcohol on 0.3 gram of metallic sodium. When the sodic methylate was first added, there was no apparent action, but after warming on the steam-bath for a few minutes a white crystalline sodium salt separated. The salt was filtered out, washed with a little methyl alcohol, dissolved in water, filtered again, and then dilute sulphuric acid added in excess, which gave a bulky white precipitate. This was filtered off, washed with water, alcohol, and ether, and then dried for a short time over sulphuric acid and paraffine. The product was analyzed with the following results: —

0.2047 gram of the substance gave by the method of Carius 0.1966 gram of argentic bromide.

	Calculated for $C_6Br_2(OCH_3)_2(OH)_2(OCH_3)_2$.	Found.
Bromine	41.03	40.88

The dibromdimethoxyquinone dimethylhemiacetal is a white amorphous solid insoluble in all the common solvents. It melts at 178°–

188°, at the same time changing to a red substance, probably dibromdimethoxyquinone. This change can also be produced by treatment with dilute sulphuric acid, or dilute hydrochloric acid. From this description of the preparation and properties of this hemiacetal it is evident that the action of sodic methylate on dibromdiphenoxyquinone is similar in every respect to the action of this reagent on the corresponding compound containing chlorine.

Action of Potassic Phenylate on Trichlorquinone.

By treating 5 grams of trichlorquinone suspended in water with two equivalents of potassic phenylate, made from 2.7 grams of potassic hydrate and 8 grams of phenol, a red semi-liquid substance was formed. After the mixture had been heated on the steam bath for twenty minutes in order to complete the reaction, the supernatant liquid was poured off, and the pasty residue washed with water by decantation, and then warmed with alcohol, which converted it into a crystalline solid. These crystals were then separated by filtration, washed thoroughly with cold alcohol, and recrystallized from alcohol containing a small amount of benzol until they showed the constant melting point 169°–170°, when they were dried at 100°, and analyzed with the following results: —

I. 0.1888 gram of the substance gave by the method of Carius 0.0818 gram of argentic chloride.

II. 0.1913 gram gave 0.0832 gram of argentic chloride.

	Calculated for $C_6HCl(OC_6H_5)_2O_2$.	Found. I.	Found. II.
Chlorine	10.87	10.71	10.75

Properties of Monochlordiphenoxyquinone. — It crystallizes from alcohol in long, slender, pointed oval blades arranged in irregular groups, — a very characteristic habit of crystallization. It has an orange color, with a slight brownish tinge, and melts at 169°–170°. It is easily soluble in benzol or chloroform; difficultly soluble in alcohol; slightly soluble in carbonic disulphide; insoluble in water, ether, or ligroine. It is easily reduced to a colorless hydroquinone by glacial acetic acid and zinc dust.

To see whether it would form a hemiacetal 0.5 gram of the monochlordiphenoxyquinone was treated with the sodic methylate made by acting on 0.3 gram of metallic sodium with a few cubic centimeters of methyl alcohol. The quinone dissolved in the cold, but, even when allowed to stand for some time and stirred vigorously, no precipitate of a sodium salt was formed. When, however, it was warmed for a few minutes, a heavy white precipitate was deposited, which, after being washed with a little methyl alcohol, dissolved completely in water, giving a clear solution. The addition of an acid to this solution produced a turbidity, which soon developed into a white precipitate, undoubtedly the hemiacetal, but this passes so easily into a red quinone derivative that we have not attempted to analyze it, especially as its properties leave no doubt as to its nature. It follows from these observations that the stability of the hemiacetals is increased by the number of negative radicals, such as chlorine atoms, present.

Action of Sodic Ethylate on Quinone.

Although the results described in the last section made it probable that the hemiacetal derived from quinone itself would be very unstable, we have tried some experiments on the action of sodic ethylate on quinone ($C_6H_4O_2$), and think it best to give a preliminary account of them here, in spite of the fact that they have not led as yet to any definite result. They have, however, proved that sodic ethylate acts on quinone, but have by no means convinced us that the product is a hemiacetal. On treating quinone dissolved in ether with an alcoholic solution of sodic ethylate, a heavy flocculent dark green precipitate is formed, which is insoluble in ether, but dissolves in alcohol or water with decomposition. This precipitate does not seem to be homogeneous, as by fractional precipitation products were obtained unlike in color, and also in their composition, as shown by analysis; moreover its study is rendered difficult by the fact that it takes fire spontaneously when dried at ordinary temperatures in the air; if, however, it is dried in an atmosphere of hydrogen, it can be exposed to the air without taking fire at ordinary temperatures, but, if warmed to 40°, it begins to glow, and burns like tinder. Before studying this rather unmanageable substance further, we tried to get some idea of the way in which the reaction ran by a quantitative study of it, based upon the fact that all the quinone can be removed from its ethereal solution by the sodic ethylate.

In the first trial, it was found that one gram of quinone required 0.2352 gram of sodium for complete precipitation.

In the second trial, one gram of quinone required 0.2460 gram of sodium.

In the third trial, 3 grams of quinone required 0.6 gram of sodium.

These results indicate that each molecule of quinone acts with only one molecule of sodic ethylate, as the amount of sodium needed in this case for one gram of quinone is 0.213 gram, and the observed results come as near to this number as could be expected, when the roughness of the method is considered. This conclusion is confirmed by the yield of the salt obtained from 3 grams of quinone, which was 4.7 grams, whereas, if only one molecule of sodic ethylate had been added to each molecule of the quinone, the yield should have been 4.9 grams. The study of other parts of this research has occupied our time so completely that we have been unable to do more on this division of the subject, but we hope that this work can be taken up again in this Laboratory at an early date.

Experiments on Phenoquinone.

It has been suggested in the introduction that phenoquinone and quinhydrone may be hemiacetals similar to those studied in this paper. In that case phenoquinone should contain two hydroxyl groups, and form salts. Accordingly, we have tried to obtain a salt of it, although the chances of success were not great as Wichelhaus * has stated that phenoquinone forms no salts, but is decomposed by alkalies. Still we thought that possibly by using sodic ethylate in insufficient quantity we might succeed, as the replacement of the hydrogen by the metal might take place in preference to the decomposition of the phenoquinone, especially as Wichelhaus also states that it gives a blue color with alkalies. We proceeded as follows. One gram of phenoquinone † was dissolved in ether, and treated with an alcoholic solution of the sodic ethylate made from 0.1 gram of sodium; as 0.154 gram of sodium would be required for two atoms of sodium to each molecule of phenoquinone, there was a considerable excess of this latter substance. As soon as the sodic ethylate was added, a heavy flocculent dark green precipitate was formed, which was filtered out, washed thoroughly with ether, and dried over sulphuric acid and paraffine. We hoped at first that this was the salt of phenoquinone, and three sodium determinations seemed to confirm this idea, as they gave 13.14, 13.41, and 14.31 per cent of sodium, which is not far from the number calculated for a sodium salt of phenoquinone, since that is 13.52 per cent of sodium; but the study of the ethereal filtrate from the salt threw a great deal of doubt on this conclusion, since it contained a large amount of phenol. We think it more probable, therefore, that the sodic ethylate decomposed the phenoquinone into quinone and phenol, and that the green salt was then formed by the action of the sodic ethylate upon the quinone, the action being the same as that described in the last section. This inference is strengthened by the marked resemblance in appearance between the salts obtained in these two cases, and also by the study of the properties of the salt made from the phenoquinone, since it dissolved completely in water, forming a dirty green solution, and undoubtedly suffering partial decomposition, as ether extracted from this solution colorless crystals of hydroquinone recognized by their melting point of 169°. The addition of an acid to this solution gave no precipitate, and upon shaking out the acidified liquid with ether, nothing was extracted but hydroquinone. If the substance had been the desired salt of phenoquinone, phenol should have been obtained from this filtrate. Although these experiments tell against the formation of salts of phenoquinone, we do not consider them absolutely final, but the study of the action of alkalies on phenoquinone under other conditions will be continued in this Laboratory during the coming college year.

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* Ber. d. ch. G., V. 248.

† The phenoquinone was made by adding one equivalent of quinone dissolved in hot ligroine to two equivalents of phenol dissolved in a small quantity of the same solvent. The mixed solutions were warmed for a few minutes, and then on cooling beautiful red crystals separated, which were purified by recrystallization from alcohol.

As we had not succeeded in making a salt of phenoquinone we next turned our attention to the action of sodic phenylate on quinone, as, if the phenoquinone is a hemiacetal, this should act as well as free phenol, whereas according to the other theories of the constitution of phenoquinone, it is hard to see how there should be any action in this case. Sodic phenylate was made by warming the proper amount of metallic sodium with a solution of phenol in benzol until the sodium had entirely disappeared. As the benzol cooled, the white crystalline sodic phenylate separated abundantly, and, after filtering, any free phenol was removed by washing with cold benzol. Upon adding the solid sodic phenylate to a solution of quinone in absolute ether a dark red crystalline substance looking like phenoquinone was formed. After evaporating off the ether slowly, the residue dissolved easily in water with a slight green color, and acids precipitated from this aqueous solution a small amount of a dark reddish solid. The ethereal solution showed a tendency to turn green round the edges during the evaporation which may perhaps have been due to the action of the moisture in the air. If benzol was used to dissolve the quinone instead of ether, a pink substance was formed, which changes to a dark green body when warmed. With ligroine as the solvent, a dark green precipitate was obtained at first. Unfortunately, this work was undertaken at the very end of the term, so that a more careful study of these products must be postponed until next year, but these preliminary experiments show that sodic phenylate does combine with quinone, and therefore lend a certain amount of countenance to our suggestion that phenoquinone is a hemiacetal.

XIX.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON THE CUPRIAMMONIUM DOUBLE SALTS.

SECOND PAPER.

By Theodore William Richards and Andrew Henderson Whitridge.

Presented May 9, 1894.

The continuation of the study of the cupriammonium double salts, begun in 1891,* has led to the preparation of the following new compounds : —

(1.) $Cu(NH_3)_2ClCHO_2$.
(2.) $Cu(NH_3)_3BrC_2H_3O_2 . H_2O$.
(3.) $Cu(NH_3)_2BrC_3H_5O_2$.
(4.) $Cu(NH_3)_2BrC_3H_5O_3$.
(5.) $Cu(NH_3)_2ClC_3H_5O_3$.

(1.) Cupriammonium Formiochloride, $Cu(NH_3)_2ClCHO_2$.

The bromide corresponding to this chloride has been described already by Richards and Shaw. The chloride itself was obtained at the same time by these experimenters, but only in an impure state, and the present problem was to determine the conditions necessary for the preparation of the substance in a state of purity.

If any considerable amount of water is present in the materials, basic salts of copper are certain to be precipitated, and to contaminate the preparation. On the other hand, the slight solubility of cupric formiate and cupriammonium chloride in alcohol makes it difficult to avoid the admixture of these substances with the desired compound, if alcohol is used in the anhydrous condition.

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* Theo. W. Richards, Berichte d. d. ch. Gesell., XXV. 1492; T. W. Richards and H. G. Shaw, These Proceedings, XXVIII. 247.

The following procedure was found to be the most successful, but great care was needed to carry it out. Three grams of crystallized cupric formiate were dissolved in just enough warm alcohol to effect solution, and two grams of ammonic chloride were added to the mixture. The whole was then heated to boiling, and dry ammonia was passed in until a very slight excess was present. Upon cooling and evaporation in the air, fine blue prismatic crystals separated, which were fairly pure, as the analyses show. The salt resembles in its properties the formiobromide, being permanent in dry air, but at once decomposed by water. In color it is a purer blue than the formibromide, having much less of the greenish tinge.

In the analysis of the compound the copper was determined electrolytically after the substance had been evaporated with sulphuric and nitric acids. The chlorine from a new portion was weighed as argentic chloride, and the ammonia was distilled after the addition of potash. The formic acid was determined by combustion.

Analyses of $Cu(NH_3)_2ClCHO_2$.

I. 0.0862 gram of the substance gave on electrolysis 0.0305 gram of copper.

II. 0.0997 gram of the substance gave on electrolysis 0.0356 gram of copper.

III. 0.1258 gram of the substance yielded 0.0994 gram of argentic chloride.

IV. 0.1285 gram of the substance yielded 0.1008 gram of argentic chloride.

V. 0.1060 gram of the substance distilled with caustic potash required 11.75 cubic centimeters of a decinormal solution for neutralization.

VI. 0.0984 gram of the substance yielded on combustion 0.0241 gram of carbon dioxide.

Analyses III. and IV. were made from different samples; hence they prove the definiteness of the compound.

	Copper.	Ammonia.	Chlorine.	Formic Acid.
I. . .	35.38			
II. . .	35.71			
III. . .	—	—	19.54	
IV. . .	—	—	19.40	
V. . .	—	18.91		
VI. . .	—	—	—	25.05
Averages	35.54	18.91	19.47	25.05

	Calculated for $Cu(NH_3)_2ClCHO_2$.	Found.
Copper	35.69	35.54
Ammonia	19.15	18.91
Chlorine	19.90	19.47
Formic Acid (CHO_2)	25.26	25.05
	100.00	98.97

(2.) AMMON-CUPRIAMMONIUM ACETOBROMIDE,

$Cu(NH_3)_3BrC_2H_3O_2 . H_2O$.

This compound is formed readily when cupric bromide is dissolved in a mixture of alcohol and glacial acetic acid, and an excess of dry ammonia gas is passed into the solution. It is essential to have the solutions concentrated. For example, 2.5 grams of cupric bromide were shaken with 13 cubic centimeters of glacial acetic acid and 25 cubic centimeters of alcohol. Upon cooling after the addition of the ammonia, which raised the temperature of the solution, the desired substance separated out. If when passing in the gas a black precipitate ($Cu_3Br_6(NH_3)_{10}$) falls after the solution has become dark purple,* the supernatant liquid should be decanted before it is allowed to crystallize. The precipitate shows the presence of an excess of cupric bromide in proportion to the acetic acid.

Ammon-cupriammonium acetobromide had already been made by Richards and Shaw; but the analyses of the compound were so unsatisfactory that no account of the substance was given in their paper. This unsatisfactoriness was due, not to any difficulty in preparing the substance in a state of purity, as in the previous instance, but rather to the great difficulty of drying the substance enough without drying it too much. The extra molecule of ammonia and the molecule of water are held very loosely, mere exposure to the air allowing them to escape. Especially is this the case when the substance is placed over sulphuric acid. 0.1242 gram of material, which had been exposed thus until constant in weight, yielded 0.0331 gram. or 26.65 per cent. of copper upon electrolysis. This showed that the substance had lost practically all of its extra ammonia and water, for the theoretical per cent of copper in $Cu(NH_3)_2BrC_2H_3O_2$ is 26.87. The new salt consists of pearly flakes of a brilliant light blue color, somewhat less intense than that of the normal cupriammonium acetobromide. It is only very slightly soluble in alcohol, and is at once decomposed by water, a little of the copper going into solution. In properties and general appearance it resembles the ammon-cupriammonium acetochloride prepared by Richards and Shaw, except that it is much less stable.

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* Richards and Shaw, *loc. cit.*

The acetic acid was determined by distillation with phosphoric acid, according to the well known method of Fresenius. Hydrobromic and a trace of phosphoric acid which come over in the distillate were precipitated with argentic nitrate from the neutralized solution, the result being calculated as argentic bromide, since this is the greater part of the precipitate.

Analyses of $Cu(NH_3)_3BrC_2H_3O_2 \cdot H_2O$.

I. 0.3276 gram of the substance yielded 0.0774 gram of copper upon electrolysis.

II. 0.3902 gram of the substance yielded 0.0896 gram of copper upon electrolysis.

III. 0.3376 gram of the substance yielded 0.2365 gram of argentic bromide.

IV. 0.2453 gram of the substance yielded 0.1732 gram of argentic bromide.

V. 0.4214 gram of the substance yielded 0.2940 gram of argentic bromide.

VI. 0.2600 gram of the substance distilled with caustic potash required 13.28 cubic centimeters of a decinormal acid solution for neutralization.

VII. 0.1528 gram of the substance distilled with caustic potash required 16.29 cubic centimeters of a decinormal solution for neutralization.

VIII. The distillate from a mixture of 0.1469 gram of the substance with phosphoric acid required 5.67 cubic centimeters of a decinormal alkali for neutralization. Approximately corrected for the alkalimetric equivalent of the argentic phosphate and bromide obtained from the distillate, this amount becomes 5.47 c.c.

	Copper.	Ammonia.	Bromine.	$C_2H_3O_2$.
I. . .	23.63			
II. . .	22.97			
III. . .	—	—	29.81	
IV. . .	—	—	30.04	
V. . .	—	—	29.68	
VI. . .	—	18.20		
VII. . .	—	18.19		
VIII. . .	—	—	—	22.35
Averages .	23.30	18.20	29.84	22.35

	Calculated for above Formula.	Found.
Copper	23.40	23.30
Ammonia	18.84	18.19
Bromine	29.42	29.84
Acetic Acid	21.72	22.35
Water (by difference)	6.62	6.32
	100.00	100.00

It is evident that most of the substance analyzed had lost some of its ammonia and water. A few other determinations were made of substance just prepared and not dried at all, in order to be sure that the atomic ratio of the ammonia to the copper was not greater than 3 : 1. This point was proved beyond a doubt.

(3.) CUPRIAMMONIUM PROPIONOBROMIDE, $Cu(NH_3)_2BrC_3H_5O_2$.

Ten grams of ammonic propionate, made by neutralizing propionic acid with ammonia gas and allowing the solution to evaporate over caustic potash, were mixed with two grams of cupric bromide, and dissolved in about fifty cubic centimeters of absolute alcohol. Dry ammonia gas was passed into the solution, and on standing a precipitate of cupriammonium bromide ($Cu(NH_3)_2Br_2$) came down. Four and a half cubic centimeters of strong propionic acid were added to dissolve the precipitate, and more ammonia gas was added. Again the same crystals appeared, showing that the tendency to form this substance was much more decided than the tendency to form the substance desired. Since the addition of more propionic acid did not help the matter, one and a half grams of precipitated cupric oxide were added, and the whole was warmed until most of the powder had dissolved. After filtration and evaporation in the air, prismatic crystals of a very strong blue color were deposited, proving to be the substance sought. The crystals were washed with alcohol, and dried in the air, in which they are permanent. 0.5750 gram of the substance was found to displace 0.2197 gram of toluol having a specific gravity of 0.8619; hence the specific gravity of cupriammonium propionobromide is 2.255. The other properties resemble so closely those of the acetic compound that it is not worth while to detail them.

Analyses of $Cu(NH_3)_2BrC_3H_5O_2$.

I. 0.1017 gram of the substance gave on electrolysis 0.0262 gram of copper.

II. 0.1061 gram of the substance gave on electrolysis 0.0270 gram of copper.

III. 0.0825 gram of the substance yielded 0.0624 gram of argentic bromide.

IV. 0.0788 gram of the substance distilled with caustic potash required 6.19 cubic centimeters of a decinormal acid for neutralization.

V. 0.1109 gram of the substance yielded 0.0588 gram of carbon dioxide upon combustion.

	Copper.	Ammonia.	Bromine.	Propionic Acid.
I. . . .	25.76			
II. . . .	25.45			
III. . . .	—	—	32.18	
IV. . . .	—	13.40		
V. . . .	—	—	—	29.31
Averages .	25.60	13.40	32.18	29.31

	Calculated for above Formula.	Found.
Copper	25.37	25.60
Ammonia	13.61	13.40
Bromine	31.90	32.18
Propionic acid	29.12	29.31
	100.00	100.49

(4.) CUPRIAMMONIUM LACTOBROMIDE, $Cu(NH_3)_2BrC_3H_5O_3$.

This compound is easily obtained by dissolving syrupy lactic acid and about a third of its weight of cupric bromide in alcohol, and then passing dry ammonia gas into the solution. Basic salts of copper do not form readily here, but if an insufficiency of lactic acid is added, $Cu(NH_3)_2Br_2$ will crystallize out. The crystals are of a strong light blue color, with a faint tinge of purple; they may be obtained of great size. They are permanent in the air, and at once decomposed by water. 2.6377 grams of the substance were found to displace 1.0334 grams of toluol, indicating a specific gravity of 2.20.

For analysis the salt was washed twice with alcohol, and pressed between filter paper.

Analyses of $Cu(NH_3)_2BrC_3H_5O_3$.

I. 0.1742 gram of the substance gave on electrolysis 0.0418 gram of copper.

II. 0.1108 gram of the substance yielded 0.0786 gram of argentic bromide.

III. 0.1916 gram of the substance yielded 0.1360 gram of argentic bromide.

IV. 0.0850 gram of the substance required on distillation 6.25 cubic centimeters of decinormal acid solution for neutralization.

V. 0.0987 gram of the substance required 7.38 cubic centimeters of decinormal acid.

VI. 0.1634 gram of the substance yielded on combustion 0.0819 gram of carbon dioxide.

Analyses II. and III. were made from different samples of the substance.

	Copper.	Ammonia.	Bromine.	Lactic Acid. $C_3H_5O_3$.
I. . . .	23.99			
II. . . .	—	—	30.19	
III. . . .	—	—	30.20	
IV. . . .	—	12.56		
V. . . .	—	12.84		
VI. . . .	—	—	—	33.79
Averages .	23.99	12.70	30.19	33.79

	Calculated for above Formula.	Found.
Copper	23.85	23.99
Ammonia	12.79	12.70
Bromine	29.99	30.19
Lactic Acid	33.37	33.79
	100.00	100.67

(5.) CUPRIAMMONIUM LACTOCHLORIDE, $Cu(NH_3)_2ClC_3H_5O_3$.

Four grams of cupric lactate were dissolved in strong alcohol, and when the solution was boiling, two grams of ammonic chloride were added. Through this solution perfectly dry ammonia gas was passed until slightly in excess. Upon filtering and evaporating the solution fine crystals of cupriammonium lactochloride were deposited. A similar method would have answered in the case of the bromine. These crystals are of a somewhat lighter blue color than the lactobromide, but otherwise their properties are similar. Because of this similarity, determinations of the chlorine and copper were considered enough to identify the compound.

Analyses of $Cu(NH_3)_2ClC_3H_5O_3$.

I. 0.1751 gram of the substance gave on electrolysis 0.0496 gram of copper.

II. 0.1341 gram of the substance gave on electrolysis 0.0382 gram of copper.

III. 0.1314 gram of the substance gave on electrolysis 0.0378 gram of copper.

IV. 0.1025 gram of the substance yielded 0.0659 gram of argentic chloride.

V. 0.1015 gram of the substance yielded 0.0656 gram of argentic chloride.

	I.	II.	III.	IV.	V.
Copper	28.33	28.49	28.76		
Chlorine	—	—	—	15.93	15.98
Average	28.52			15.95	
Calculated for above formula	28.64			15.96	

Attempts were made to make similar compounds of butyric acid without success. Various different proportions, suggested by those required in the previous preparations, were tried with equal failure, and the attempts were finally discontinued.

It was also hoped that such compounds as $Cu(NH_3)_2ClNO_3$ and $Cu(NH_3)_2NO_3 . C_2H_3O_2$ might be found. The results of a great many experiments showed that under ordinary conditions nothing but $Cu(NH_3)_2Cl_2$, or $Cu(NH_3)_4(NO_3)_2$, can be obtained. Further attempts to combine cupriammonium sulphate with cupriammonium acetate were also unsuccessful; so that in these directions the field seems to be limited. All of these facts, as well as the relative properties of those compounds which have been prepared, may be of some use in the future when the structure of the cupriammonium compounds comes under consideration. Work upon the subject, as well as upon similar investigation of products containing amines instead of ammonia, is being continued here.

Cambridge, Mass., September 20, 1894.

XX.

CONTRIBUTIONS FROM THE CRYPTOGAMIC LABORATORY OF HARVARD UNIVERSITY.

XXVI. — NOTES ON LABOULBENIACEÆ, WITH DESCRIPTIONS OF NEW SPECIES.

By Roland Thaxter.

Presented November 23, 1894.

Laboulbenia pilosella Robin.

(*Traité du Microscope*, p. 912, Fig. 285.)

Through the kindness of Professor Giard the existence of a species bearing this name has been brought to the writer's attention, and an examination of the figure which accompanies its description leaves little doubt of its identity with the form described by the writer on European specimens of the genus Lathrobium under the name *Acanthomyces brevipes*. The plant figured by Robin is said by him to occur on a member of the same genus, and his drawing, though coarse, corresponds so closely in essentials that the two may be considered synonymous. In selecting the name Acanthomyces, however, the writer was not aware of its previous use by Lebert in a zoölogical publication, the *Acanthomyces aculeata* * of this writer having escaped the notice of compilers in recent years. In view of this fact a new designation for the genus of Laboulbeniaceæ becomes necessary, and the writer would suggest for this purpose the name *Rhachomyces,* from the resemblance which the main axis of these plants bears to a vertebral column. The new name will therefore include the six described species, *Rhachomyces longissimus*, *R. lasiophorus*, *R. hypogæus*, *R. Lathrobii*, *R. furcatus*, and *R. pilosellus* (Robin), to which may be added a seventh form, parasitic, like *R. hypogæus*, on a blind cave beetle.

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* Zeitschr. f. wissensch. Zoologie, 1858, Vol. IX. p. 447.

RHACHOMYCES nov. nom. = ACANTHOMYCES THAXTER.

RHACHOMYCES SPELUNCALIS, nov. sp.

Perithecium more or less deeply suffused with brown; short and stout, with a broad bluntly rounded apex. Receptacle slender, the main axis constricted strongly at the septa, its cells rather small, the basal slender and cylindrical; the remainder, about nine in number, all evenly and rather deeply suffused with brown, and more or less uniform in size. Appendages mostly opaque, more or less rigid, hyaline-tipped, those surrounding the base of the perithecium hardly equalling it in length, a few lower on the receptacle exceeding its apex by the whole length of the plant: of the shorter median appendages some are terminated by a peculiarly modified partly hyaline (antheridial?) cell, the neck-like tip of which curves strongly outwards, terminating bluntly. Perithecia 90 × 37 μ. Receptacle about 110 μ (when not proliferous). Longest appendages 300 μ. Total length to tip of perithecium 185 μ to 260 μ (in proliferous forms).

On *Anophthalmus pusio* Horn. West Virginia.

The smallest species of the genus, more nearly allied to *R. lasiophorus* in the form of its perithecium and the disposition of its appendages around the base of the latter. It is quite distinct, however, from any of the described species.

DIPLOMYCES, nov. gen.

Flattened antero-posteriorly, sub-triangular, bilaterally symmetrical, furcate through the presence of a pair of prominent posterior projections. The receptacle consisting of two superposed cells, followed by four cells placed antero-posteriorly in pairs, of which the posterior produce the characteristic prominences; the anterior a pair of short stalked perithecia, near the base of which, within and above, arise two or more pairs of appendages, and eventually a second pair of perithecia. Appendages copiously branched, many of the branchlets terminated by beak-like cells. Spores once-septate.

A singular genus, recalling Teratomyces, to which it seems most nearly allied through the presence of the characteristic terminal beak-like cells of its appendages. The branching of the latter is not, however, sympodial in a single plane, as is the case in Teratomyces, and the general structure of the receptacle is difficult to homologize with that of any other genus. The second pair of perithecia arise in all probability from secondary divisions of the pair of perithecia-bearing cells above described; but the exact structure in this region, behind the stalk cells of the perithecia, has not been made out satisfactorily. An obliquity in the septum which separates the basal and sub-basal cells sometimes results in the apparent absence of any sub-basal cell.

DIPLOMYCES ACTOBIANUS, nov. sp.

More or less faintly tinged with brownish. Basal cell of receptacle triangular, sub-basal cell flattened or wedge-shaped; the posterior prominences peculiar to the genus nearly as long as the receptacle itself, slightly divergent, two-celled, the terminal cell twice as long as the basal, tapering slightly towards its rounded extremity. On the anterior side the two perithecigerous cells bear the first pair of perithecia on short stalk-cells bent abruptly upwards, divergent, and succeeded by three small cells forming the base of the perithecium. The perithecia rather slender, curved towards the receptacle so that their tips project beyond it, divergent, rather long and slender, tapering slightly, the apex blunt with ill defined lips, the base of the old trichogyne persisting conspicuously below the pore. Appendages branching, arranged in pairs symmetrically like the perithecia; a smaller one arising just behind the stalk cell of the perithecium, a much larger one above this followed by a few smaller ones less definitely arranged in the region whence a second pair of perithecia may arise. All the appendages more or less copiously branched, the branchlets terminating in many cases by the slender, curved and sharply pointed cells characteristic of Teratomyces. Spores 32 × 2 μ. Perithecia, including stalks, about 75 × 12 μ. Receptacle to tips of prominences 75 μ. Total length to tip of perithecia 110 μ. Greatest width 37 μ.

On *Actobius nanus* Horn. Massachusetts.

This species occurs rather rarely on the abdomen of a large brown variety of *Actobius nanus*, but not as far as has been observed on the normal form. A second form, perhaps distinct from the present, was found on the abdomen of a small Philonthus, and is distinguished by the presence of slender thread-like branches from the larger appendages. Sufficient material of this form was not, however, obtained, and it may prove to be nothing more than a variety of the one above described.

SPHALEROMYCES OCCIDENTALIS, nov. sp.

More or less evenly tinged with brownish. Perithecium large, subfusiform, with faintly defined ridges at the divisions between the wall cells, the apex made externally oblique through the outgrowth of one of the lip cells which forms a pointed projection beyond the pore; the stalk cell wholly free, tapering to a narrow base, and about as long as the receptacle proper. Receptacle small, pointed below, its sub-basal cell united throughout its length to the basal cell of the appendage, its basal and sub-basal cells separated by a horizontal septum. The appendage straight, rigid, tapering, composed of a series of usually four superposed cells separated by oblique partitions, and bearing short branches with flask-shaped antheridia from their upper inner angles. Perithecia 200 × 45 μ. Length to tip of perithecia 350 μ. Length to tip of appendage 200 μ. Length of receptacle 55 μ.

On *Pinophilus densus* Lec. Utah.

The occurrence of a second well marked species, abundantly distinct from the type, serves to settle any doubts which may have existed concerning the validity of this genus. The present form was found on the abdomen of its host, and is readily distinguished from *S. Lathrobii* by the peculiarly modified tip of its perithecium, as well as by other important differences.

LABOULBENIA HAGENI, nov. sp.

More or less deeply tinged with brown. Perithecium slightly inflated, tapering to the blunt outwardly oblique apex, which is blackened below the hyaline lips. Appendages arising from an outer and an inner basal cell, the outer of which is followed by a squarish cell of about the same size, from the end of which project four rather short, rigid, slightly divergent hyaline branches, which taper to blunt tips, and, as a rule, hardly exceed the tip of the perithecium: the inner basal cell gives rise to two squarish cells, one on either side, each of which bears usually a pair of branches similar to those just described. Receptacle short and stout, normal in form, the lower portion of the basal cell hyaline. Perithecia 55 × 18 μ. Appendages (longest) 65 μ. Total length to tip of perithecium 100 μ.

On *Termes bellicosus* var. *Mozambica* Hagen. Africa.

The occurrence of a most typical and decidedly insignificant looking species of this genus on a larva of the worker of a species of white ant is certainly quite unexpected in view of the wide difference which exists between this Neuropterous host and the usual insects infested by the genus. But for the four stiff branches arising from the sub-basal cell of the outer appendage, and suggesting the roots of a molar tooth, it would be difficult to specify its distinguishing characters. The species is dedicated to the memory of the late Professor Hagen, by whom it was observed many years since on the same specimen examined by the writer, collected by Dr. Peters in Africa, from all parts of which sufficiently abundant material was obtained.

LABOULBENIA KUNKELII (GIARD).

Thaxteria Kunkelii GIARD, Comptes Rendus Hebdomadaires des Séances de la Société de Biologie, Sér. IX., Vol. IV. p. 156.

Through the kindness of Professor Giard, the writer has had an opportunity of examining specimens of this remarkable species, which is by far the largest member of the family, measuring between three and four millimeters from its base to the tip of the perithecium. It occurs with the succeeding species on the elytra and thorax of *Mormolyce phyllodes* Hagenb., a carabid beetle, native in the East Indies. The writer is unable to agree with Professor Giard in believing that this form, however singular, should be separated generically from Laboulbenia, to which it seems to correspond in every essential detail. The type of cell arrangement, so characteristic in Laboulbenia, is followed without deviation; while the appendages also originate in a manner much more typical than is found in very many species of this genus. The elongation of the basal wall cells of the perithecium to form a stalk-like base finds also an exact parallel in species like *L. Galeritæ*, *L. longicollis*, *L. melanotheca*, and other forms, the generic reference of which is not to be disputed.

LABOULBENIA PALMELLA, nov. sp.

Perithecium nearly straight, almost opaque, sometimes slightly inflated, its tip nearly symmetrical, truncate, its inner walls often having a corrugated appearance, the four lower wall cells elongated and contracted to form a short stalk below and about one third as long as the ascigerous portion. Appendages arising from two small basal cells: *an outer* which gives rise to a series of two or three opaque branches placed antero-posteriorly, the inner of which alone reaches any considerable size, branching sympodially in an antero-posterior plane, the main axis opaque, successively inflated below the branchlets which are usually about ten in number, opaque with hyaline tips: *an inner* which gives rise to a single branch on either side consisting of a subcylindrical basal cell, black below, nearly hyaline above and followed by a series of sympodial branchlets like those of the outer appendage. Receptacle short, tapering rapidly to the base, wholly black and opaque with the exception of the whole or a portion of its basal cell which may be hyaline and is abruptly bent above the very large hoof-like haustorium or blackened point of attachment. Spores 150 × 12 μ. Perithecium 580 × 75–100 μ, its neck 75–150 × 35–65 μ. Receptacle 300–400 μ, its greatest width 75–100 μ. Appendages (longest) 500 μ, the branchlets about 225–250 × 7–8 μ. Total length to tip of perithecium, 1–1.1 mm.

On *Mormolyce phyllodes* Hagenb. Perak, Molucca, Java.

The writer is indebted to Professor Riley for abundant material of this species found by Mr. Schwarz on a specimen of Mormolyce in the National Museum labelled "Java," as well as to Mr. Beutenmueller who has kindly sent material derived from a specimen in the Central Park Museum labelled Molucca. Professor Giard has also most generously allowed him to examine the original specimen of Mormolyce from Perak on which the types of *L. Kunkelii* were associated with the present species. The two species are very closely allied, and were found intermingled towards the base of the elytra, although the smaller was much more abundant on the flattened margins where it presents the appearance under a hand lens of a grove of little palm-trees. The absence of any transitional forms between the two species seems to render it unlikely that they should prove merely varieties of a single form, while the much smaller size of *L. palmella*, its wholly opaque and short receptacle, straight short-necked perithecium, large hoof-like base, together with the absence of furcation in the main axis of the two lateral branches of its inner appendage, afford constant and sufficient specific differences. The antheridia appear to be represented by flask-shaped bodies borne on short hyaline branches near the tips of the branchlets of the inner appendages. The trichogynes are well developed and more or less copiously branched.

LABOULBENIA MELANOTHECA, nov. sp.

Tinged with pale reddish brown, except the nearly black perithecium. Perithecium long, straight, symmetrical, subcylindrical or but slightly inflated, narrowed abruptly to the symmetrical apex, its basal wall cells elongated to form a neck-like stalk about one fourth as long as its main body, projecting from the receptacle at an angle to its long axis towards and beyond the appendages. Appendages as in *L. mexicana*, hardly exceeding the perithecium in length, consisting of two basal cells; the outer producing an outer and an inner branch either simple or once branched; the inner producing single branches on either side. Receptacle elongate expanding very gradually from the base, distally abruptly rounded and contracted below the insertion cell on one side and the neck-like base of the perithecium on the other. Spores 95 × 5.5 μ. Perithecium 220–245 × 60–65 μ, its neck-like base about 75 × 30 μ. Receptacle about 515 × 100 μ. Total length to tip of perithecium 800–835 μ.

On *Galerita mexicana* Chaud. Nicaragua.

This species has been previously referred to by the writer as a possible hybrid between *L. mexicana* and *L. Galeritæ*. It seems on more careful comparison, however, to be abundantly distinct from either. The neck-like base of the perithecium appears to be formed from the elongated basal wall cells of the perithecium which lie wholly below the ascogenic cells. The eight types were found on the elytra of their host in company with *L. mexicana*.

Laboulbenia decipiens, nov. sp.

Perithecium nearly opaque, not punctate, large, slightly and evenly inflated, tapering rather abruptly to the nearly symmetrical apex; the basal wall cells forming a short stout clearly defined neck; the septa separating the upper wall-cells deeper blackish and spirally twisted. Appendages arising as in *L. Galeritæ* from a conical cellular base consisting of one outer and two inner rows of superposed cells, each of which bears a single simple straight septate branch, its lower segments slightly inflated, hardly exceeding the tip of the perithecium. Antheridia blackish, with a very long curved neck, borne singly or two together from the sub-basal cell of the inner series of superposed cells. Receptacle as in *L. Galeritæ* except that cell (3) extends upwards nearly to the black insertion cell of the appendages, cells (4) and (5) being wholly included by it. Color sub-hyaline with brownish suffusions especially in the region of cells (4) and (5). Perithecium 175–278 × 55 μ (smallest 130 × 37 μ), its stalk-like base 40–55 × 30 μ. Receptacle (larger) 300 × 75 μ.

On *Galerita æquinoctialis*. Guatemala.

This species is remarkable for its close resemblance to *L. Galeritæ*. It is at once distinguished by the position of cell (3), and by the peculiar twist of its perithecial wall cells which are not punctate as in the latter species.

Laboulbenia Aspidoglossæ, nov. sp.

Perithecium black, almost opaque, rather narrow, the inner margin curved abruptly outwards to the rather large apex, its lips very oblique outwards. Appendages arising from two basal cells which are nearly equal in size: the outer inflated and separated from the cell above it by a blackened septum, this sub-basal cell roundish, inflated, about as large as the basal cell and giving rise to two branches, an outer and an inner; the outer separated from it by a blackened septum and consisting of a basal cell with three terminal branchlets the inner of which is deeply and broadly blackened at its base, while the other two are wholly hyaline and fertile: the inner branch from the sub-basal cell has no blackened basal septum and produces several short branchlets bearing numerous antheridia. The inner appendage, like the outer, consists of a roundish or squarish basal cell separated from a sub-basal cell by a blackened septum; the sub-basal cell producing a tuft of short branches bearing at their tips two to four antheridia or becoming more elongate and sterile. Receptacle normal, the two basal cells rather slender, elongate, colorless; the distal cells suffused with blackish brown. Perithecia 110–120 × 40 μ. Appendages (longest) 240 μ. Total length to tip of perithecium 333 μ, greatest width 63 μ.

On *Aspidoglossa subangulata* Chaud. Kansas (M. A. Barber).

A species clearly marked by the peculiarities of its appendages, which, unlike almost all other species of the genus, are fertile without regard to their external or internal origin.

LABOULBENIA MACROTHECA, nov. sp.

Amber-yellow. Perithecium large, evenly inflated, the curvature from base to apex nearly symmetrical on either side, the apex rather large, outwardly oblique, with a blackish basal shade; the remainder of the perithecium translucent, amber-colored, the walls thick, the spore mass large. Appendages flexuous, thick, pale amber-colored or tinged with purplish, arising from two cells, the inner small and roundish, the outer much larger, two or three times as long, usually bearing a single cell with two terminal more commonly simple branches; the inner producing two branches each several times branched: the outer appendages especially more or less constricted at the septa. Receptacle small, usually short and slender, the basal cell long, narrowed towards its base, the sub-basal cell short, the remaining cells relatively small. Perithecium 130–150 × 45–55 μ. Spores 60 × 5.5 μ. Appendages (longer) 185 μ. Receptacle 150–165 × 35–40 μ. Total length to tip of perithecium 240 μ (longest 270 μ), greatest width 55–60 μ.

On *Anisodactylus Baltimorensis* Say. Maine. On *Anisodactylus sp.*? Bathurst, N. B. (H. M. Richards).

This species occurs not rarely on the anterior legs of its host, less frequently on the borders of the elytra. It may be distinguished by its pale amber color, large evenly inflated perithecium, and slender receptacle, the distal portion of which is relatively unusually reduced.

LABOULBENIA TERMINALIS, nov. sp.

Perithecium deeply suffused with smoky brown, slightly inflated, the inner margin evenly curved outwards, the outer more nearly straight, but bent abruptly outwards to the large prominent apex, the lips of which are well defined and outwardly oblique. Appendages arising from two basal cells, a very large outer and much smaller inner: the outer giving rise to two cells each of which bears terminally from two to three long slender tapering flexuous branches tinged, at least basally, with reddish brown: the inner bearing a single cell as a rule followed by two terminal cells which give rise to groups of two or three rather slender sessile antheridia: insertion cell placed just below the middle of the perithecium. Receptacle pointed below, broad above, nearly hyaline or evenly tinged with brownish, cell (7) slightly prominent below the perithecium. Spores 55 × 5.5 μ. Perithecia 120–150 × 45–50 μ. Receptacle 200–220 μ. Total length to tips of perithecium 275–340 μ.

On *Pterostichus luctuosus* Dej. Maine and Massachusetts.

This species occurs in tufts at the tips of the elytra or abdomen, apparently never elsewhere. It is allied to forms of *L. polyphaga* and *L. Pterostichi*, from which it is at once distinguished by its perithecium.

LABOULBENIA RIGIDA, nov. sp.

More or less deeply tinged with olive-brown. Perithecium becoming almost or quite opaque, somewhat inflated, a slight depression at its base above the more or less bulging terminal portion of the receptacle, its apex stout, snout-like, bent slightly inwards. Appendages arising from two basal cells, the outer of which gives rise to a single simple rigid branch, tapering slightly or not at all; the inner producing two similar somewhat shorter branches almost invariably simple and bearing near the base solitary sessile antheridia. Receptacle normal, sometimes rather elongate. Spores 75 × 55 μ. Perithecia 125–150 × 10 μ. Appendages (longest) 300 μ. Receptacle 185–300 μ. Total length to tip of perithecium (largest) 300 μ.

On *Pterostichus patruelis* Dej. Maine and Massachusetts.

This species may be distinguished by its rigid habit, straight single outer appendage and the blunt snout-like apex of its perithecium. It is one of the less well marked types of the genus, yet sufficient material from the two localities mentioned indicates that its characters are sufficiently well marked to warrant its specific separation from other species of the *flagellata* type.

LABOULBENIA CONFUSA, nov. sp.

Becoming deeply suffused with smoky brown. Perithecium rather small, inwardly inflated, the apex broad, slightly oblique outwards. Appendages arising primarily from an inner and outer cell: the outer bearing a second cell which bears terminally a dense tuft of hyaline flexuous tapering more or less divergent branches which are themselves more or less branched: the inner basal cell becoming several times divided and giving rise to numerous branches densely crowded and similar to the external ones. Receptacle consisting of a long sub-cylindrical basal cell, the sub-basal cell shorter and broader, cells (3–5) unusually large, causing this portion of the receptacle to bulge outwards in an evenly rounded and characteristic fashion. Perithecia 166 × 55 μ. Appendages (longest) 150 μ. Receptacle 215 μ long, its basal cell 90–110 × 25–40 μ. Total length to tip of perithecium, 315 μ; greatest width 75 μ.

On *Bembidium sp.* Connecticut.

This species although based on scanty material seems quite distinct from its nearest allies, *L. luxurians* and *L. compacta.* Although the general arrangement of the appendages is similar in the present species, their flexuous divergent tapering habit is quite different from those of the two forms just mentioned, from which it is also distinguished by its larger size and peculiarly shaped receptacle. It occurs on the legs of a very small metallic-green Bembidium.

LABOULBENIA CORNUTA, nov. sp.

Dark blackish brown. Perithecium tapering to a broad blunt apex, from which projects a prominent straight dark brown appendage, unicellular, bent abruptly outwards from its base, tapering slightly to its nearly hyaline rounded tip. Appendages as in *L. luxurians*, the branches fewer and stouter. Receptacle short, expanding somewhat abruptly above the sub-basal cell, the basal cell becoming narrowed and nearly hyaline towards its base. Perithecium 85 × 29 μ. Its appendage 26 × 7 μ. Total length to tip of perithecial appendage 185 μ, greatest width 52 μ.

On *Bembidium complanulum* Mann. Washington (Miss Parker).

The five types of this singular species are all in poor condition, the appendages being, for the most part, broken; but it seems safe to describe it without regard to the termination of its appendages, since the terminal projection from the perithecium distinguishes it from all other known members of the genus, and finds a parallel only in *L. Gyrinidarum*, with which it can by no chance be confused. It was found on two specimens of the host, in each case growing in a definite position towards the base of the right elytron. The beetles were among material kindly collected for the writer by Miss A. M. Parker.

LABOULBENIA OBERTHURI Giard (in lit.).

Nearly hyaline except the brown or smoke-colored perithecium and sub-basal cell of the receptacle. Perithecium large, inflated towards the base, the narrower distal half abruptly rounded and contracted below a rather narrow apex with protruding lips bent outwards; general color dark brown, much deeper below the apex. Appendages numerous, crowded, slender, short, the lower segments inflated, arising as in *L. Guerinii*. Receptacle elongate, consisting of a short curved stout nearly hyaline basal cell, a very long sub-cylindrical sub-basal cell smoky brown in color with deeper brown wart-like or scale-like scattered prominences of varying size, the remaining cells normal except that the insertion cells of the appendages are irregularly divided. Perithecium 300–315 × 120 μ. Receptacle 1 mm.–900 μ; its sub-basal cell 370–425 × 65–75 μ. Total length to tip of receptacle 1.225 mm.

On *Orectogyrus heros*, Reg. Madagascar.

This fine species has been kindly communicated to the writer by Professor Giard, who has dedicated it to M. René Oberthur, its discoverer. It is with the exception of the two species described above on Mormolyce by far the largest of the Laboulbeniæ, and is closely allied to the form already known on Gyretes (*L. Guerinii* Rob.), from which, however, it is abundantly distinct.

HEIMATOMYCES DISTORTUS, nov. sp.

Pale yellowish, more or less clavate in general form. Perithecium inflated, its external margin strongly curved, becoming abruptly constricted below a long slender tubular terminal mouth, which is usually, but not always, bent abruptly outwards almost at right angles to the nearly straight inner margin of the perithecium. A short straight bluntly pointed rather stout appendage arises on one side only of the perithecium, just below this tubular apex beyond which it projects. The basal and sub-basal cells of the receptacle about equal in length, the latter broader: distal portion of the receptacle composed of the usual four cells, the sub-terminal cell forming a distinct external prominence below the terminal cell which is bent towards and partly overlaps the perithecium. Perithecium (main body) 60 × 18 μ, its tubular apex 18–25 × 6 μ. Spores 20 × 3 μ. Length of receptacle 110 μ.

On *Laccophilus maculosus* Germ. Connecticut.

A singular species appearing at first sight malformed or abnormal. It occurs in company with *H. appendiculatus* on the anterior legs of its host.

HEIMATOMYCES UNCIGERUS, nov. sp.

Pale yellowish. Perithecium moderate, rather broad, its outer edge straight, its upper fourth free from the receptacle, its prominent bluntly tipped extremity bent abruptly outwards at right angles: a slender hooked appendage arises from a point close to the receptacle about two thirds of the distance from the base to the apex of the perithecium, projecting from it obliquely outwards. Basal cell of the receptacle large and long, the sub-basal cell small, sub-rectangular, flattened: the distal portion composed of the usual four cells, the terminal one not very prominent and bent strongly towards the perithecium. Perithecia 80 × 22–25 μ. Spores 45 × 4 μ. Perithecial appendage about 22 μ long. Receptacle 132 μ long. Total length to tip of perithecium 135 μ.

On *Laccophilus maculosus* Germ. Connecticut.

The more or less wedge-shaped apex of the perithecium of this very distinct form projects outwards abruptly at right angles to the straight outer perithecial margin. The hook-like appendage is quite unlike that of any other species in form and position, and, occurring only on one side, is not seen unless the perithecium lies at the right. It occurs with *H. spinigerus*, *H. hyalinus*, and rarely *H. marginatus*, on the posterior legs of its host.

HEIMATOMYCES SPINIGERUS, nov. sp.

Brownish yellow. Perithecium small, its tip slightly exceeding that of the receptacle; its extremity blunt, lobed, curved outwards, and bearing two projections just below the tip, unequal in size, one of which extends outwards beyond the perithecial margin as a blunt prominence. Basal cell of the receptacle often bent, expanding distally, much longer than the flattened sub-basal cell: the distal portion of the receptacle with greatly thickened external walls, and consisting of the usual four cells, the terminal one short, with a broad base and bent towards the apex of the perithecium. Three small cells are distinct below the perithecial cavity, from the outer of which is produced externally a prominent spur-like process. Perithecia 55 × 15 μ. Total length to tip of perithecium 88–90 μ. Spur-like process 12–30 μ long.

On *Laccophilus maculosus* Germ. Connecticut.

Distinguished from all other species by the spur-like process from the base of the perithecium. The septa are all defined with unusual clearness, the external walls being greatly thickened. Apparently among the rarest of the twelve species inhabiting this host.

DICHOMYCES PRINCEPS, nov. sp.

Nearly hyaline, becoming slightly and uniformly tinged with pale reddish brown, sometimes narrowly edged with blackish near the base. Receptacle large, consisting of a single small squarish basal cell, above which are three successive transverse rows of cells placed side by side, the upper margin of each series convex: the lower series consisting of a long narrow axial cell, with three or four more or less obliquely superposed cells on either side: the middle series consisting also of an axial cell, with five to eight cells on either side, which extend obliquely upwards and outwards to form a free rounded projection, each cell of which bears a short bladder-like appendage, the antheridia prominent at the base of each projection: the third or distal transverse series like the second, the cells often slightly more numerous, forming projections in a similar fashion on either side which bear the same bladder-like appendages. The axial cell of the terminal series is followed by two small cells, each bearing a short appendage, on either side of which a large somewhat flattened cell forms the base of the perithecium. Perithecia two, more or less divergent, elongate, slightly inflated and tapering gradually to the blunt apex. Perithecia 110–165 × 22–30 μ. Spores 38 × 4 μ. Receptacle 150–180 × 70–75 μ.

On *Philonthus sordidus* Grav. Massachusetts.

A conspicuous species, occurring on all parts of the host, but especially on the inferior surface of the abdomen.

EUCANTHAROMYCES, nov. gen.

Receptacle consisting of two superposed cells, giving rise on one side to a free stalked perithecium, on the other to a free appendage. The appendage consisting of a basal and sub-basal cell terminated by a compound antheridium. The antheridium formed from numerous small cells, obliquely superposed in three rows, bordered externally by a sterile cell and terminated by a cavity from which the antherozoids are discharged through a short irregular finger-like projection.

EUCANTHAROMYCES ATRANI, nov. sp.

Pale straw-colored. Perithecium rather long, slightly inflated, tapering to a blunt apex with rounded lips, its stalk consisting of a single large free basal cell surmounted by three smaller cells. Basal and sub-basal cells of the receptacle long and very obliquely superposed, lying almost side by side. The appendage consisting of a basal cell not wholly free, but partially connected with the stalk cell of the perithecium at its base, followed by a second sub-triangular cell, the oblique upper walls of which separate it on the inside from the body of the antheridium proper, and on the outside from the long narrow cell which forms its sterile outer margin. Antheridium subcylindrical, with rounded apex consisting of three series of obliquely superposed cells decreasing in size from below upwards, and running obliquely upwards and outwards, the lower series of six cells, the middle of four, and the upper of two, the three series terminating in a common cavity filled with antherozoids, which are discharged through a terminal irregular finger-like projection which is bent strongly outwards. Perithecium 135 × 35 μ. Length to tip of perithecium 260 μ. To tip of antheridium 150 μ.

On *Atranus pubescens* Dej. Virginia (T. Pergande).

Two specimens of this perplexing form were found in company with *Rhachomyces lasiophorus* on an example of Atranus kindly sent me by Mr. Pergande. The genus is based wholly upon the peculiar compound antheridium, which seems quite different in character from that of either Cantharomyces or Camptomyces, its nearest allies.

CERATOMYCES MIRABILIS Thaxter.

Abundant material of this species, collected in Maine and Massachusetts, indicates that the writer has confused two closely allied forms which were at first considered merely varieties of a single species. The type of *C. mirabilis,* which is the most common species, is characterized by a stouter perithecium, the inner margin of which is strongly curved, the curve being broken by a rounded prominence on either side just below the apex, which is bent strongly to the base of the perithecial appendage. The perithecial appendage is evenly and distinctly inflated towards its base, and reaches a considerable length. The main axis of the antheridial appendage is short and stout, consisting of about a dozen superposed cells. From this type may be separated a second species, which may be designated as follows: —

CERATOMYCES CONFUSUS. nov. sp.

General habit and color as in *C. mirabilis.* Perithecium hardly inflated, its inner margin curving evenly to the prominent blunt apex which stands out free from the base of the perithecial appendage. The perithecial appendage shorter than in *C. mirabilis,* without the bulbous inflation at its base. Axis of antheridial appendage long and slender, distally attenuated, with comparatively few short branches. Receptacle as in *C. mirabilis.* Spores 75 × 3.7 μ. Perithecia 235–335 × 65 μ. Axis of antheridial appendage 235 μ (longest). Receptacle 165 × 75 μ.

On *Tropisternus glaber* Hb. and *T. nimbatus* Say. New England.

This species is much rarer than *C. mirabilis,* and is at once distinguished by the absence of any prominences below the apex of the perithecium, as well as by the differences presented by its perithecial and antheridial appendages. Otherwise the two species are easily confused.

INVESTIGATIONS ON LIGHT AND HEAT, MADE AND PUBLISHED WHOLLY OR IN PART WITH APPROPRIATION FROM THE RUMFORD FUND

XXI.

EXPERIMENTS AND OBSERVATIONS ON THE SUMMER VENTILATION AND COOLING OF HOSPITALS.

By Morrill Wyman.

Presented November 23, 1894.

In this climate, the sick in our hospitals often suffer much distress from the excessive heats of summer. Their relief demands more serious attention than it has generally received.

At first sight it would seem a simple matter by means of the cooling processes known to the arts to surround a sick bed with a cool atmosphere; but this atmosphere must be constantly renewed and the incoming air as constantly cooled; this cooling is a difficult problem, and has not been satisfactorily solved by any of these processes. It is much easier to warm our patients in winter than to cool them in summer.

The three principal ways in which our bodies lose heat are by convection, radiation, and evaporation; but they are efficient in very different degrees.

Radiation, although effective in the open air with a clear sky, does us but little good as a cooling agent on a warm and muggy day. In our wards, when their walls are near the temperature of our patients, or rather of their clothing, which is really the radiating surface, radiation benefits them but little, for these walls of necessity return nearly as much heat as is radiated to them. Neither is radiation sensibly modified by any movement of the surrounding air.

Convection, as the name implies, is the carrying away of heat; it increases inversely as the temperature of the surrounding air, and directly with its moisture and velocity. We know well the agreeable sensations on a hot summer's day of the sea breeze, which in a greater or less degree combines these qualities. We know too how much, on a still, hot day, fanning, which changes neither the moisture nor the temperature of the air, but simply causes more air to move over and come in contact with us, adds to our comfort by displacing the hot and moist air immediately around us.

The Cambridge Hospital is warmed by air heated in passing over pipes in which hot water circulates, enclosed in heating boxes; it is obvious that the substitution of cold water for hot water in these pipes would cool, more or less, the air on its way to the wards.

It was thought worth while to determine by experiment what influence this previous cooling might have on the comfort of our patients as compared with air of the same velocity from the open, unchanged in temperature or moisture.

An *air-chamber* extends under the whole ward; it is devoted exclusively to the purpose of receiving the air for ventilation and distributing it equally through the heating boxes and ten registers to the ward above. This air-chamber is well lighted, and is kept scrupulously clean; nothing is allowed to be placed in it under any pretence whatever. It is generally cooler in the summer than the atmosphere; water from the city water service is also cooler by several degrees, in the early summer, than the air. By connecting the city main with the pipes in the heating boxes, and allowing the water flowing through them to run to waste, they become in some degree air-coolers.

On the 21st of May, 1893, all windows and openings in the air-chamber were carefully closed, and the water from the main let on. At 3 P. M. the external thermometer was at 84° F.; there was no wind, and the patients were suffering from the heat. The temperature of the air-chamber was 67° F.; the water as it entered the cooling boxes, 57–58°. The electric fan, 36 inches in diameter, driving the air into the air-chamber, was put in motion, making 500 revolutions with an air-moving power of 10,200 cubic feet a minute. At 4 P. M. the air entering the ward at the registers was at 71° F.

During this hour 400,000 cubic feet of air, as measured by a Casella's air-meter, was thrown into the ward through the ten registers; a quantity sufficient to fill the ward of 21,000 cubic feet twenty times an hour, — once in three minutes.

The result was satisfactory; the comfort of the patients was manifestly improved.

But it must be observed that the cooling surfaces were, first, the ten cooling boxes of 30 square feet each at 57–58° F., and, secondly, the floor and walls of the air-chamber, the two together amounting to about 3,300 square feet. The temperature of these walls could not well be determined; but as they had not been exposed to much increase of heat since the winter, they may be assumed to have been about that of the water supply, then 58° (in winter it is about 50°). At the outset then we had the air-chamber full of cool air and a cooling surface of about 3,000 feet along which the air, driven by the fan, was diffused before it entered the ward. The cooling power of the boxes may be assumed to be about one tenth that of the walls.

These were the arrangements through the month of May, with the same benefit to the patients. In June, the summer heats were greater and more constant, and the fan more steadily used. The temperature of the air-chamber and the air passing through it had increased, and that of the water had already risen to 70°, and is usually somewhat higher later in the season; the quantity of water required was large and expensive; it was therefore shut off permanently. The same amount of ventilation, however, was continued, and the conditions as to the air-chamber and the admission of the air to the ward were unchanged. During the summer, the ward temperature gradually rose until it differed but little from that of the open air.

Still the comfort given to our patients and their nurses under both these methods was immediate and decided. To those entering the ward there was a feeling of freshness and freedom of air quite beyond that of the other ward of similar construction, which had only the usual summer ventilation.

At first the walls of the air-chamber to a degree acted as coolers, but this ceased as they became warmer.

We may form some estimate of the probable effect of the boxes as coolers in summer, by comparing it with their work as heaters in winter.

The average boiler temperature in December and January is 200° F.; that of the return, 145°; therefore, 55° of heat is lost in heating 120,000 c.f. of air hourly supplied to the wards in winter.

From these data Professor Trowbridge has kindly made the following computation: —

“Mean temperature of water $= 172.5°$ (173°)
“ “ “ air $= \frac{1}{2}(30 + 70) = 50$
Mean excess of water temperature available $173–50 = 123$
Excess per degree rise of air temperature $\frac{123}{40} = 3.07$

“To cool the same amount of air from 80° to 70° (mean temperature 75°) would require, if Newton’s law hold, a mean temperature of $75° — 10 \times 3.07 = 45°$ approximately.”

Our boxes, therefore, as then constructed, with a water circulation at 58° F., were inadequate to our purpose as cooling boxes. It is true the boxes could be enlarged. It has been computed that, with a constant flow of cool water at 50° through boxes 5.6 times as large as those we now have, we might keep a ward at 70° with an outside air of 90°, and a ventilation reduced to 40,000 cubic feet an hour, — one third of our winter supply, or one tenth of our summer supply. But we have no reliable experiments to confirm this computation. Our own experiments have shown that this previous cooling of the air is an expensive and uncertain process, and would lessen the evaporation upon which, as we shall see further on, we principally depend for cooling, and, what is more important, would probably not be hygienic. No further experiments were made as to cooling the air before its entrance into the ward.

Our first experiment showed clearly enough the advantage of a large supply of fresh and slightly cooled air; but it is not so clear how much was due to the temperature of the air, and how much to the rapid evaporation caused by its velocity and dryness. But as the comfort of the sick continued the same after the rise of temperature of the cooling apparatus and the shutting off of the cold water, it is probable that it was due more to the velocity and drying qualities of the air acting upon the *patients themselves*, than to any change of temperature in the ward generally, which, as we have already said, differed but little from that of the open air. This is a point of the first importance.

The most effective way of losing heat is that last mentioned, that is, by evaporation. It is Nature's great consumer of heat. Evaporation increases with the temperature of the air, with its dryness, and with its velocity. Common observation teaches how rapidly wet clothing and muddy roads dry in windy weather. If we are exposed to a warm dry air, especially if it is in motion, we may feel cool, or even cold, because of the rapid evaporation from the skin. In the heats of summer the relative dryness of the air is of more importance to our comfort than its temperature. The thermometer and our sensations do not correspond. It is evaporation increased by the air put in motion by his punkah that enables the Englishman to bear the heats of India and keep his blood at its normal temperature.

Pettenkofer calculates that in twenty-four hours we lose heat, by respiration alone, as follows: —

In dry air at 32° F.	293,044 units of heat.
" " 86°	274,050 " "
A difference of about	19,000 " "
In air completely humid at 32°	265,050 " "
" " " " 86°	105,390 " "
A difference of nearly	160,000 " "

The cooling by respiration in moist air is therefore about one eighth of that in dry air at the same temperature. But this is not all the heat lost by evaporation, nor the greater part; the loss by the skin is nearly twice that by the lungs under the same conditions. Here also the same law holds, the greater the relative moisture the less evaporation and consequently the less cooling.

According to Lavoisier and Seguin, 900 grams of fluid per day are discharged by perspiration, and 500 grams from the lungs, making 1400 grams of fluid lost in twenty-four hours. The evaporation of this quantity of water will consume 750 units of heat, or about one fifth of all the heat produced in the body in twenty-four hours.

The production of heat in the animal body, and its maintenance at a normal standard, are two of the most important processes in the living organism. The two chief means for regulating the temperature of the body are the skin and the lungs. Of these the most direct and simplest is that by the cutaneous perspiration. The relations of these organs to the atmosphere, therefore, are of great importance in the question now under consideration.

But the rate of evaporation and consequent cooling depends in great measure on the aqueous vapor already in the atmosphere. That this relative amount has a material influence on our individual comfort there is no doubt. It is certain that on those days when the proportion of humidity is greatest, even the healthiest feel an oppression and languor, and that on other days when the humidity is less there is an exhilaration of spirits and an increase of muscular energy.

It is worth while, then, to recall the laws governing this aqueous vapor, for it pervades the atmosphere, is one of the main causes of its movements, and the only fluctuating ingredient in its composition.

The evaporating power of air raised to a higher temperature is increased. A quantity of air absolutely humid at 59° F. holds an amount of vapor equal to $\frac{1}{80}$ of its weight; at 86°, $\frac{1}{40}$; at 113°, $\frac{1}{20}$; at 140°, $\frac{1}{10}$; so that while the temperature advances in an arithmetical progression, the vapor-diffusing power of the atmosphere rises with the accelerating rapidity of a geometrical series having a ratio of two; with the same ratio, evaporation increases, and consequently the cooling process.

It is upon this play of forces in the aqueous vapor and the air, and the movements they bring about, that we must rely for the comfort of our patients in the heats of summer. It is not a question of changing the temperature of the air; practically, we cannot alter that nor its humidity, in the volumes required for ventilation. It is a question of the rate of evaporation from a perspiring surface, which again is governed in great measure by the velocity of the air; and this by the improvements in the arts we can control.

If, on the other hand, we attempt to attain our object by cooling the air before it enters the ward, we are met with this fact. If air absolutely humid comes in contact with warmer air also saturated, the latter will be cooled, it will approach the dew-point, and, if its moisture is condensed into visible vapor, will give out heat. Evaporation consumes heat, condensation liberates heat.

In our first experiment the previous cooling of the air did not bring it to the point of condensation, but its relative humidity was increased; the rate of evaporation was therefore diminished, and to that degree it was a disadvantage.

The quantity of air required for our purpose cannot, as we have already said, be determined by instruments of precision alone; it must be learned by experiment and the declared sensations of the sick.

The movement of the air around us, and it is never still, — the natural ventilation as it is called, — is much greater than is generally supposed. Repeated experiments have shown that at two feet a second we first feel the air as a moving body; less than that we consider a perfect calm. And yet at this velocity air would move from end to end of our ward of 60 feet in 30 seconds, and across it in half that time, quite unnoticed by us.

To give comfort during the excessive heats of summer the sick require three or four times the air needed for satisfactory ventilation in winter. It required 400,000 cubic feet an hour for our sixteen patients, and yet while this large quantity was passing through the ward it was only known, except at the registers, by the accompanying sense of freshness and pleasant coolness; it was never felt as a draught.

"The great regulator of the heat of the body is undoubtedly the skin." Physiology teaches that perspiration is a secretion, in a sensible or insensible form, constantly going on. Increased heat increases perspiration, and the evaporation of this increased quantity consumes in work a large portion of the heat derived from the atmosphere, and thus prevents an undue rise of the temperature of the bodily organs. The very intensity, therefore, of the peripheral circulation, under the action of heat, leads the way to relief.

Experiments made more than a hundred years ago prove that, if the skin perspires freely and the perspiration be readily evaporated, the temperature of the body may remain nearly normal in an excessively hot atmosphere, — even more than 200° F.

In the present atmosphere of mixed air and aqueous vapor, with which it is never saturated, evaporation and convection must coexist. So long as the expired air is loaded with moisture, and the skin performs its perspiratory function, and the movement of the surrounding air is under our own control, if, so to speak, we own a breeze, we may confidently rely on our ability to dispense its comforting and refreshing influences to the patients in our hospital.

The following observations with the wet and dry bulb thermometer may serve to illustrate the cooling of a moist surface. June 17, 1894, a thermometer in a still room was at 78° F.; after covering the bulb with a piece of thin cotton cloth moistened with water, and fanning it for five minutes with a common fan, it fell to 72°, — a difference of 6°. The same thermometer on the same day at 99°, treated in the same way, fell to 77°, — a difference of 12°. A thermometer in the open air in the shade, July 13, 1894, with a gentle breeze, was at 95°; with a moistened bulb, at 73°, — a difference of 12°. The relative humidity at the same time was 53%.

But the air must be in motion. A perspiring patient in still air is surrounded by an atmosphere permeated by much aqueous vapor; this must be diffused and carried away from the neighborhood by the continued arrival of fresh drier air, to get the full cooling effect due to evaporation.

It is in this way that simple agitation of the air in a warm still room brings relief, as with a common fan, or the rotary fan of the shops, or the Indian punkah. So it is with a ride in the open electric car on a hot day; the relief is immediate. There is no atmospheric change either in temperature or in moisture; it makes no difference whether we move through the air, or the air moves by us, the sense of cooling is the same. In both, we are surrounded by air constantly renewed, bringing with it the pleasurable sensations and invigorating influences belonging to a freely moving atmosphere.

What these influences are to those in health we know; what they are to those languishing on beds of sickness, those only who have experienced them can fully appreciate. That the patients in our hospital have derived much comfort from them, their repeated declarations fully prove. Besides the physical comfort they give, — like the suggestions of flowers and music, with which the sufferings of the sick are now so often soothed, — these large volumes of air fresh from the fields seem to hold up to the mind of the convalescents suggestions of other scenes, which displace, for the time at least, present surroundings, and encourage the hope, so helpful to the sick, of a speedy return to their former enjoyments.

The experience of the Cambridge Hospital leads to these two conclusions: first, that fresh air directly from the open, in the quantity and manner there supplied, can be made to give great comfort to the sick during the heats of summer; and, secondly, that previous cooling of the air so supplied is difficult and practically useless.

To this may be added, what is of much importance to charity hospitals, that the method here adopted is the least expensive of the cooling processes hitherto made generally known.

INVESTIGATIONS ON LIGHT AND HEAT, MADE AND PUBLISHED WHOLLY OR IN PART WITH APPROPRIATION FROM THE RUMFORD FUND.

XXII.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

XLIII. — EXPERIMENTS ON THE RELATION OF HYSTERESIS TO TEMPERATURE.

BY FRANK A. LAWS AND HENRY E. WARREN.

Presented by Charles R. Cross, October 10, 1894.

THIS paper gives an account of some experiments to determine the effect of temperatures much above the normal on the dissipation of energy by hysteresis in a specimen of steel.

At the time of the beginning of this research, in February, 1894, there were no complete studies of this subject known to us. A casual reference is to be found in the Proceedings of the American Institute of Electrical Engineers, Vol. VII. p. 325, 1890, by Prof. Harris J. Ryan. The tests there referred to were made on a cast-iron ring. The maximum temperature employed was 360°. The details of the measurements are not given. A short paper by Dr. Wilhelm Kuntz appeared in the Electrotechnische Zeitschrift, Vol. XIII., May 6, 1892. In this Dr. Kuntz showed that the hysteresis loss decreased with rise of temperature. A second paper by the same author appeared in the Electrotechnische Zeitschrift, Vol. XV., April 5, 1894. The magnetometer method was used by Dr. Kuntz in this work. In this paper tests of several ferrous materials are given, as well as some on a specimen of nickel.

At the outset of this research it was decided that alternating currents should be used, and that the losses should be determined by a Wattmeter, thus reducing the time required for observations to a minimum. The instrument which we designed and used is shown in Figure 1. We have decided to call the arrangement a Watt-balance. Mr. A. E. Kennelly has given in the Electrical Engineer, December 21,

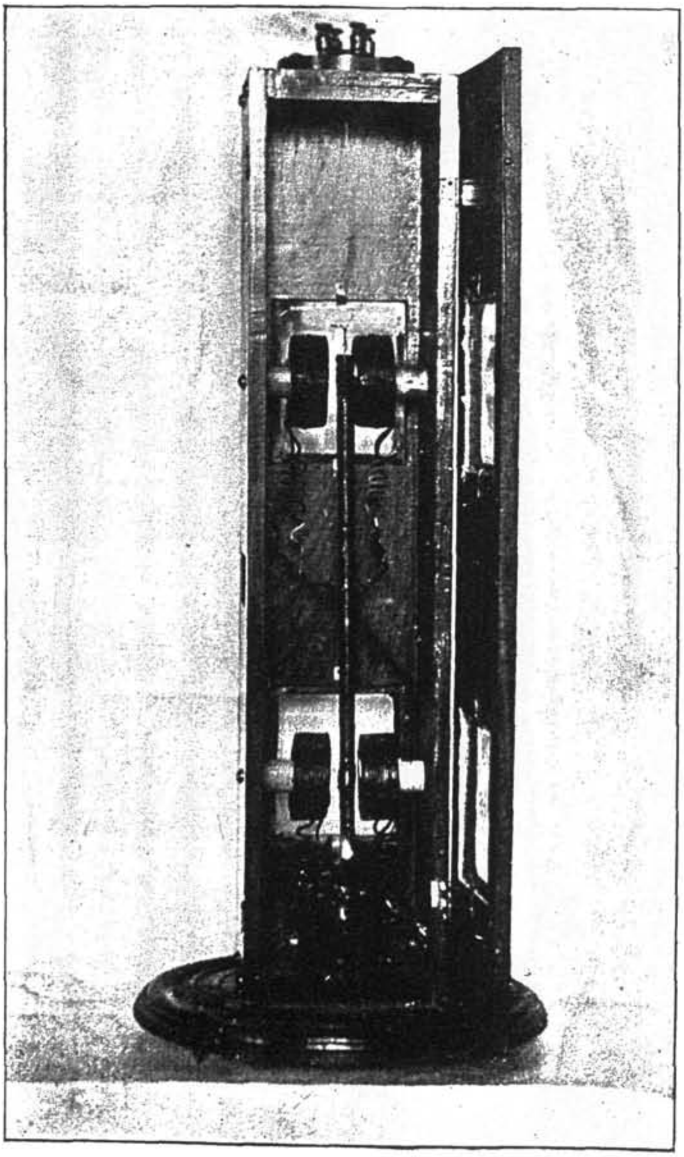

FIGURE I.

1892, a description of a "Differential Wattmeter." This instrument gives the difference of the mean values of two definite integrals representing the primary and secondary energy in a transformer; that is, the losses. The Watt-balance measures the ratio of the mean values of two definite integrals. It can therefore be used to measure the efficiency of a convertor, giving the result by a single reading.

The Watt-balance consists of two electrodynamometer Wattmeters, one above the other. The movable coils are rigidly connected in our instrument by a spiral-wound paper tube, and consist of 100 turns of silk-covered German silver wire No. 32 B. & S. gage. The resistance, including leads, is [illegible]03 ohms; the diameter of coils, 2 cm. In series with the movable coils are two adjustable resistances, r_1 and r_2, as shown in Figure 2. The stationary coils are arranged in pairs; each is 2.3 cm. in mean radius, and contains 130 turns of No. 12 cotton-covered wire. They are movable along their axes, so that the factor of the instrument may be adjusted. The vertical distance between the two dynamometers is 30 cm. The movable parts are suspended by a silk thread inside a narrow paper tube to prevent disturbance by air currents, and directive force is given by four spiral springs, made of copper wire 0.005 cm. in diameter. These springs serve as leading in wires for the movable coils. The instrument is read by a telescope and scale.

In Figure 2 is shown the scheme of connections for a hysteresis test. At the left the slide resistances for controlling the currents are shown. By the proper insertion of the connection, *C*, either a direct or an alternating current could be sent through the remainder of the apparatus, which in the main circuit consisted of an electrodynamometer, one pair of stationary coils, the specimen under test, a known resistance, *R*, of German silver strip immersed in kerosene oil to keep it at a constant temperature, and the second pair of fixed coils. At one terminal of *R* a connection was made by means of a short piece of stout wire and a key, *K*; beyond the key the circuit branched, passing through the adjustable resistances r_1 and r_2, the proper movable coils, and returning one lead to the external terminal of the specimen, and the other to the corresponding terminal of *R*. The resistance r_1 was some hundreds of ohms, seldom falling below 300, and was more frequently in the neighborhood of 1,000; r_2 was kept at a constant value, 976 ohms. The resistances r_1 and r_2 were ordinary plug boxes, and the assumption was made throughout the work that the resistances of circuits r_1 and r_2 were so high in comparison with their inductances that no correction factor need be applied to the indications of the

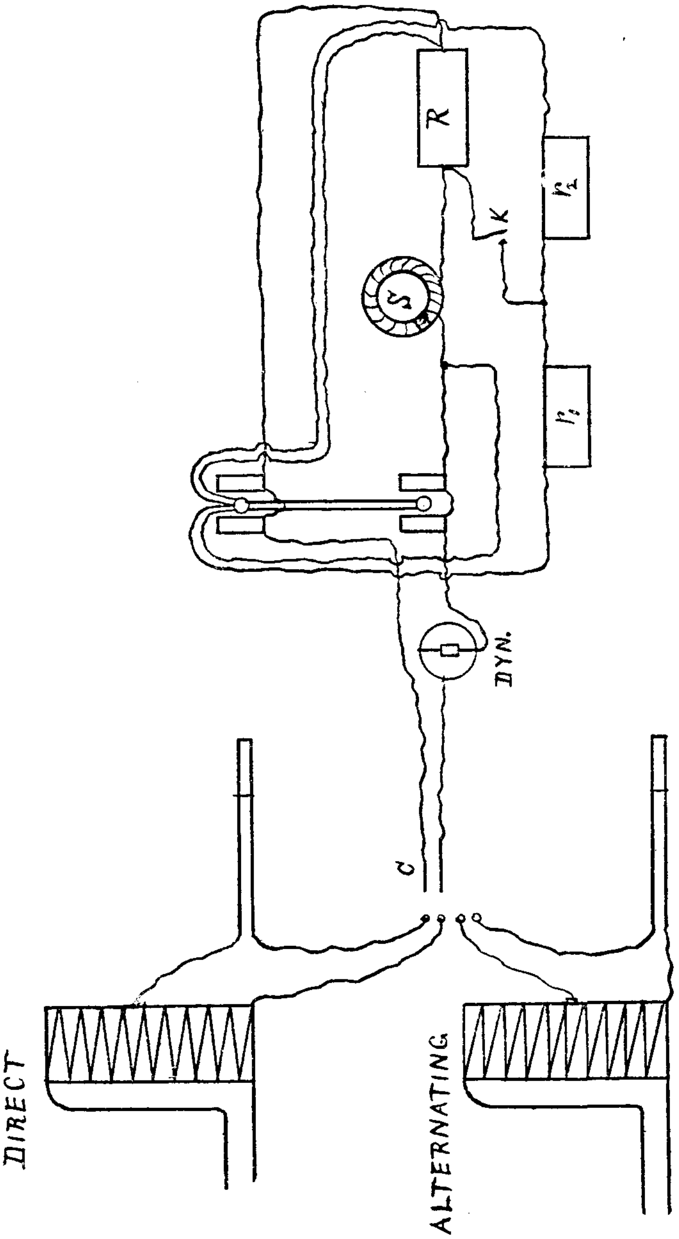
R
r_2
K
S
r_1
DYN.
c
DIRECT
ALTERNATING

FIG. 2.

Watt-balance. It may be well to mention that the use of high resistances constructed in the usual way by double winding may lead to serious errors in alternating current measurements on account of the capacity effects.

If the plug C be inserted so that a current flows in the apparatus, and no deflection is observed, then the factors of the upper and lower dynamometers are equal; if the key K is depressed, there will in general be a deflection, which may be reduced to zero by adjusting r_1, as a zero reading means that the average values of the products of the currents in the two coils of the upper and lower dynamometers are the same. It is known that the work in S bears the same ratio to the work in R that the total resistance in circuit r_1 does to the total resistance in circuit r_2. If the current is alternating, the work in S is of course divided between hysteresis and heating losses. No allowance has been thought necessary for the work done in the suspended coils. If W_S and W_R represent the work in the specimen and in R, then

$$W_S = W_R \left(\frac{r_1 + 103}{r_2 + 103} \right) = \frac{I^2 R \, (r_1 + 103)}{r_2 + 103},$$

I^2 is given by the electrodynamometer DYN.

To correct for the heating loss in S a direct current of any convenient magnitude is sent through the circuit, and a second balance, r_1^1, obtained,

$$R = 1{,}079 \text{ ohms. } r_2 = 976 \text{ ohms; so } W_S = \frac{I^2}{1000} (r_1 - r_1^1).$$

It will be seen that the Watt-balance as used in the present case is a Wattmeter with an electrodynamic control. The advantage derived from obtaining this control by shunting a portion of the main current is that any manipulation of the circuits does not disturb the equilibrium of the instrument, and that it renders it possible to use the instrument in a null instead of a compensation method.

As the hysteresis loss is a function of the maximum magnetization, denoted by B, it was necessary to provide some means by which the maximum might be kept constant, and its value determined. The device sketched in Figure 3 was used for this purpose. In addition to the magnetizing coil, the specimen was provided with a winding of 24 turns, which was connected in series with an adjustable resistance of 874 ohms during the tests, and a galvanometer of 126 ohms. Leads were carried to the dynamo room, and terminated in brushes which rested on the edge of an ebonite disk 11 inches in diameter, fastened rigidly to the dynamo shaft; the brushes were carried by a radial arm, the motion of which is controlled by a small magneto-motor driven by three Leclanche cells. The motor was governed by a reversing key in the testing room, about one hundred feet away. The alternator used had ten poles, thus making the length of a wave 72°. A piece of brass, 36° or one half a wave long, was set into the edge of the disk, and the whole carefully trued up. When the dynamo was in action the B current was closed once during a revolution, and for a time corresponding to one half a wave length. The galvanometer then performs the operation

$$\frac{2}{T}\int_{t^1}^{t^1+\frac{T}{2}} C\,d\,t$$

fifteen hundred times a minute. The value of this integral will be a maximum when it extends over the time between $+B$ and $-B$. By

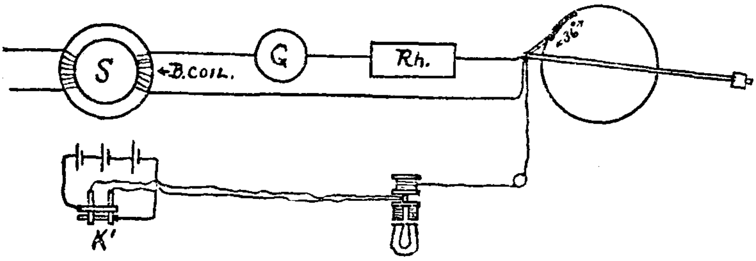

FIG. 3.

the use of the key K^1 the brushes may be shifted, and the reading of the galvanometer brought to its greatest value. With the dynamo running at its normal speed a Leclanche cell. E.M.F. 1.4 volts was inserted in the circuit; $R\,h$ was 1,374 ohms, and the deflection 21.2 cm.; with brushes short circuited and $R\,h$ equal to 14,874 ohms the deflection was 21.8 cm., the ratio of deflection being .972. If the brushes made perfect contact, and there was no self-induction effect, the ratio would be unity, the entire cycle of operation being performed in a time short compared with the period of the galvanometer. During the tests the reading with $R\,h = 1{,}374$ was frequently repeated in order that the brushes might be kept in as uniform a condition as possible.

Owing to the manner in which the specimen is constructed, the area included in the B winding is but partially occupied by the iron. In calculating the approximate values of B no allowance has been made for this, as the permeability is high in the cases where B has been determined. If observations were taken at temperatures where the permeability was very low, it would be necessary to apply a correction for this unoccupied area. The values of B were calculated by the formula

$$B = \frac{E^1 R D}{20 A N n R^1 D^1}.$$

D is the deflection corresponding to the value of B to be found. R is the resistance in circuit $R h$; N, the number of turns on B winding. n, the number of revolutions per second. A is the area of the iron included in the B windings. D^1 is the deflection of the galvanometer when an E.M.F. of magnitude E^1 and a resistance R^1 are inserted in the circuit $R h$, the dynamo turning at the normal rate.

The furnace used for heating the specimen was built of fire brick, the external diameter was about 36 inches, height 18 inches. Inside the fire brick was a layer of asbestos wool 2½ inches thick, kept in place by asbestos board, which was protected by thin sheet iron. The box containing the specimen was made of asbestos board about 1½ inches in thickness, and lined with retort cement. During the tests it was tightly closed. The furnace was heated by three blast jets made of gas pipe, the external tubes were ¾ inch inside diameter, the inner tube ⅜ inch. The supplies of gas and air were regulated by slide valves. The jets were directed into the furnace tangentially and with a slight upward inclination, the effect being to establish a good circulation and keep the interior of the furnace at a uniform temperature.

The specimen upon which the following tests were made was composed of so called French steel, which showed on analysis the following impurities: —

Manganese	0.535	per cent.
Phosphorus	0.013	"
Silicon	0.085	"
Sulphur	0.018	"
Carbon	0.970	"

The mass of iron employed was 628 grams. From this material, which was four one-thousandths of an inch thick, rings of 3 inches' outside and 2 inches' inside diameter were stamped, and the specimen formed by piling them. Each was insulated from its neighbors by a layer of pipe clay, applied as a sort of paint, the clay having been moistened with alcohol. Every tenth layer was insulated with mica. The pile so formed was wrapped with asbestos cloth, and the magnetizing coil of 36 turns of No. 14 copper wire wound on. The wire was insulated by winding it with asbestos twine. Interwound with the magnetizing coil was the B coil of 24 turns. These two windings formed on the outside of the specimen a single layer. The temperatures were determined by a Le Chatelier pyrometer, calibrated by known melting points. The hot junction was placed inside the asbestos wrapping resting against the iron, the leads were brought out through the usual double-cored fire clay tube; this was surrounded by a piece of gas pipe thoroughly wrapped in asbestos cloth, because in using this pyrometer in a case like the present, where the leads pass from the hot junction through a space at a higher temperature at a short distance from the junction, it is necessary to guard against conduction along the leads, and consequent errors in the temperature.

The manner of making the tests and the subsequent calculation was as follows. Owing to the construction of the furnace, the specimen being well shielded from the heat of the flames by the internal chamber, the air insulation, and its own asbestos covering, the temperature of the iron rises gradually; consequently the specimen will be at very nearly a uniform temperature. When a reading is desired, the alternating current is turned on and the B deflection adjusted to its maximum value by K^1, and to its correct numerical value by varying the magnetizing current. Watt-balance resistance r_1 is now adjusted, and the pyrometer reading corrected for zero, and dynamometer reading and time observed; after a few minutes the observations are repeated, the temperature having risen in the mean time. This process is kept up until the iron loses its magnetism. Occasionally, a direct current was sent through the apparatus and the Watt-balance, dynamometer, and pyrometer readings taken; these allow the value of r_1^1 in the hysteresis formula to be determined by making a plot, the co-ordinates being Watt-balance and pyrometer readings, from the plot the value of r_1^1, corresponding to any pyrometer reading may be read off. The electrodynamometers were calibrated by sending a direct current through them, and measuring the P.D. at the terminals of a known resistance by projection against the E.M.F. of a Clark cell; the values of deflections and currents squared were plotted, giving straight lines. I^2 was determined by reference to these plots. The zero errors of the dynamometers employed were very variable, and were determined after each reading.

The results of the measurements will now be given. They are plotted as referred to at the beginnings of the several tables.

TABLE I.

First Heating: Ascending Curve.

See Figure 4.

$B = 1970$. $n = 125$. W_H = Hysteresis loss in specimen.

W_H.	Temp. °	W_H.	Temp. °
.852	23	.678	387
.834	45	.523	440
.845	67	.450	481
.845	98	.331	546
.817	132	.241	595
.809	181	.130	672
.818	272	.088	709
.742	347		

The specimen lost its magnetic properties so rapidly that further measurements could not be taken on the ascending curve.

TABLE I. — Descending.

W_H.	Temp. °
.0	787
.161	576
.206	503
.255	445
.290	417

Power shut off.

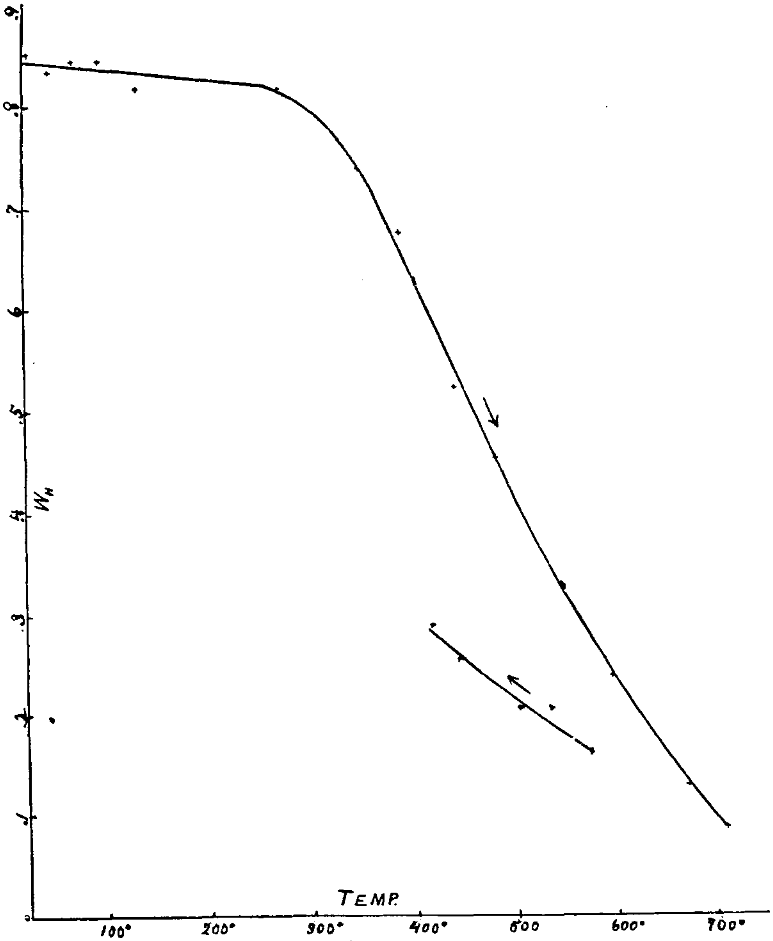

Fig. 4.

TABLE II.

SECOND HEATING: ASCENDING.

See Figure 5.

$B = 1974. \quad n = 125.$

W_H	Temp. °	W_H	Temp. °
.516	20	.149	632
.520	75	.121	653
.519	108	.115	662
.522	160	.093	679
.440	269	.083	688
.407	310	.094	692
.378	345	.104	693
.340	397	.130	693
.321	423	.130	693
.311	438	.142	693
.293	470	.144	693
.258	511	.142	692
.228	555	.140	694
.167	593		

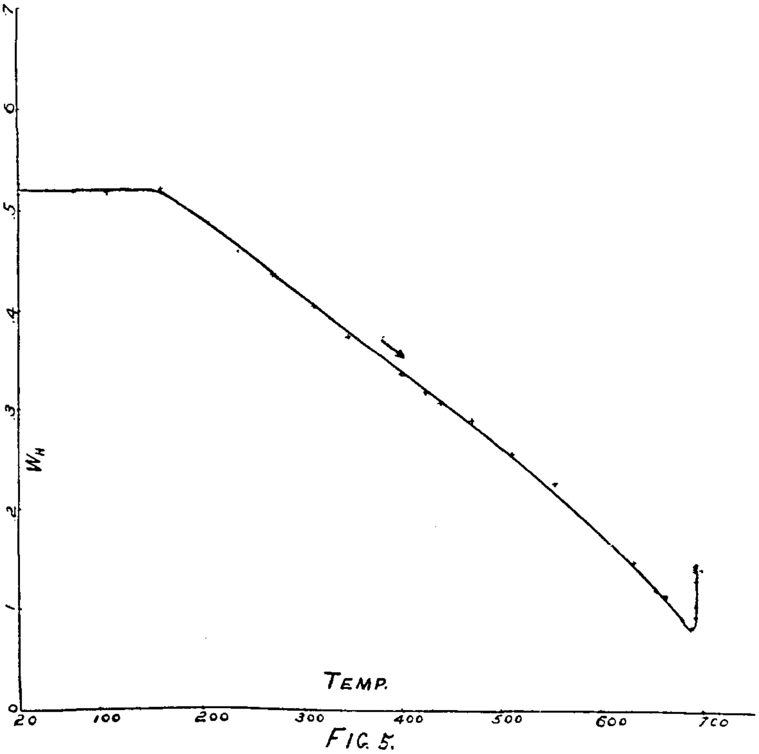

FIG. 5.

Inspection of the plots shows (Figs. 4 and 5) that for this sample of steel a moderate elevation of temperature up to about 270° has but a small influence on the hysteresis loss; that at this point a change takes place, and the diminution of hysteresis, with rise of temperature, is much more rapid, the decrease being such that at 675° the loss is but 13 per cent of its value at ordinary temperatures. After heating above the inflection point, the specimen shows on cooling a marked decrease of the hysteresis loss from its value at the same temperature on the ascending curve. If the specimen be heated again, a change of direction of the curve takes place, but at a lower temperature. The second plot (Fig. 5) shows an increase of the hysteresis loss after the point of inflection has been reached. As only two heatings were made, we were unable to verify these observations, the results of which became apparent only when they were reduced. In addition to the experiment at high temperatures, the following observations were made. A specimen was made up and the loss measured at the ordinary temperatures; a mean of three measurements gave .289 Watts as W_H. The specimen was then covered with a mixture of solid carbonic acid and ether; a mean of three measurements showed W_H as .288 Watts, showing that there is practically no change of hysteresis for a diminution of temperature to about —80°.

Between the ascending and descending observations of the second heating, readings were taken for the purpose of finding whether the temperature at which the iron becomes markedly magnetic on cooling is the same as that at which the sudden diminution of the magnetic properties occurs on heating. Simultaneous readings of the *B* galvanometer and pyrometer were taken, the current remaining constant, no adjustment for maximum was made. The readings, together with some from the descending curve of the first heating, are given below, and, after being corrected for zero, are plotted in Figure 6.

TABLE III.

First Heating.		Second Heating.	
B Reading.	Pyr.	*B* Reading.	Pyr.
38.8	7.17	28.1	6.99
38.8	7.10	29.9	7.01
38.8	7.05	31.0	7.02
38.8	7.00	32.1	7.03
38.7	6.95	33.4	7.05
38.55	6.90	34.8	7.10
38.15	6.83	36.1	7.11
37.70	6.80	37.2	7.12
37.00	6.73	37.9	7.13

First Heating.

B Reading.	Pyr.
36.3	6.69
33.65	6.51
31.2	6.45

Second Heating.

B Reading.	Pyr.
38.3	7.14
38.6	7.15
38.7	7.15
38.6	7.19
38.8	7.14
38.75	7.10
38.75	7.03
38.7	7.01
38.65	6.98
38.55	6.95
38.25	6.93
37.85	6.90
37.1	6.85
36.5	6.84
34.1	6.76
32.7	6.73
30.7	6.70

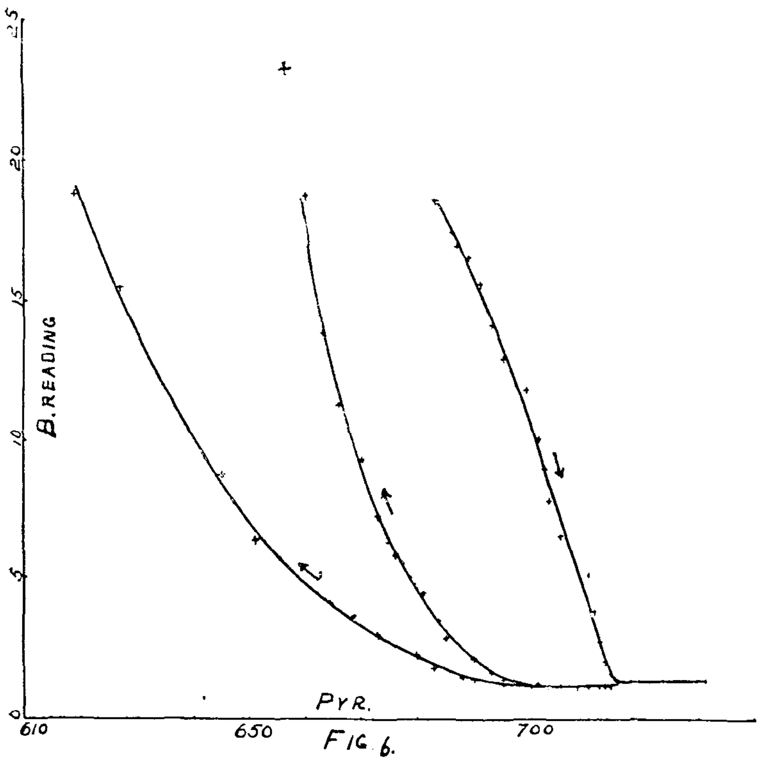

FIG. 6.

Figure 6 shows that the two points do not coincide, that on the descending being about 12° lower than that on the ascending curve. The difference of form of the curves is noticeable, showing that the regaining of magnetic properties on cooling is more gradual than their loss on heating; the sudden exaltation of magnetic properties occurs at the same temperature in the first and second coolings.

At the time of this writing the research has not been fully completed. We are, however, now engaged on further experiments, and hope to present additional data in the near future.

Rogers Laboratory of Physics,
June, 1894.

PROCEEDINGS.

Eight hundred and sixty-seventh Meeting.

May 9, 1894. — ANNUAL MEETING.

The PRESIDENT in the chair.

The Corresponding Secretary read the following letters: from the Royal Society of London, on the project of making a catalogue of scientific papers by means of international co-operation; from the Royal Society of Canada, inviting the Academy to send delegates to its Twelfth General Meeting on the 22d of May; from Ad. de Marignac, announcing the death of his father, Jean Charles Galissard de Marignac, a Foreign Honorary Member of the Academy: and from Francis M. Green and W. C. Sabine, acknowledging their election into the Academy.

Voted, To accept the invitation of the Royal Society of Canada, and the President was authorized to appoint a delegate.

The Report of the Council of the Academy was read and accepted.

The Reports of the Librarian, of the Treasurer, and of the C. M. Warren Committee were read and accepted.

Notice of a proposed change in the statutes was given by Charles L. Jackson, viz. to increase the number of Vice-Presidents so as to have one from each Class. This proposal was referred to a Committee consisting of C. L. Jackson, S. H. Scudder, and F. W. Putnam.

The President appointed, as a Committee of Co-operation on the project of making a catalogue of scientific papers, C. L. Jackson, H. P. Bowditch, and Denman W. Ross.

H. P. Bowditch presented a motion in regard to independent nominations for the offices of the Academy, which was referred to the Committee on the changes in the statutes.

On the recommendation of the Committee of Finance, it was

Voted, To make the following appropriations from the income of the General Fund for the ensuing year: —

For the library	$1,200
For general expenses	2,500
For publications	1,800
For the expenses of meetings . . .	200

Voted, That the assessment for the ensuing year be five dollars.

Voted, That $1,000 from the Rumford Fund be placed at the disposal of the Rumford Committee, to be expended in aid of investigations on Light and Heat, payments to be made on the order of the Chairman of the Committee.

In accordance with the recommendation of the Committee on the proposed alteration of the statutes, it was

Voted, To amend Chapter V. of the Statutes by changing the numbers of sections 4, 5, and 6 to 5, 6, and 7, respectively, and inserting a new paragraph as follows: —

> "4. The C. M. Warren Committee, of seven Fellows, to be chosen by ballot, who shall consider and report on all applications for appropriations from the income of the C. M. Warren Fund, and generally see to the due and proper execution of this trust."

The following gentlemen were elected members of the Academy: —

Walter Gould Davis, of Cordova, to be an Associate Fellow in Class II., Section 1 (Geology, Mineralogy, and Physics of the Globe), in place of the late William H. C. Bartlett.

Hermann Eduard von Holst, of Chicago, to be an Associate Fellow in Class III., Section 3 (Political Economy and History).

Ingram Bywater, of Oxford, to be a Foreign Honorary Member in Class III., Section 2 (Philology and Archæology), in place of the late Benjamin Jowett.

Sir John Robert Seeley, of Cambridge, to be a Foreign Honorary Member in Class III., Section 3 (Political Economy and History), in place of the late Charles Merivale.

The annual election resulted in the choice of the following officers: —

Josiah P. Cooke, *President.*
Augustus Lowell, *Vice-President.*
Charles L. Jackson, *Corresponding Secretary.*
William Watson, *Recording Secretary.*
Eliot C. Clarke, *Treasurer.*
Henry W. Haynes, *Librarian.*

Councillors.

William R. Livermore,
Benjamin O. Peirce,
Benjamin A. Gould,
of Class I.

Henry P. Walcott,
Benjamin L. Robinson,
Henry W. Williams,
of Class II.

Andrew M. Davis,
Thomas W. Higginson,
James B. Thayer,
of Class III.

Member of the Committee of Finance.

Augustus Lowell.

Rumford Committee.

John Trowbridge,
Erasmus D. Leavitt,
Benjamin O. Peirce,
Edward C. Pickering,
Charles R. Cross,
Amos E. Dolbear,
Benjamin A. Gould.

C. M. Warren Committee.

Francis H. Storer,
Thomas M. Drown,
Charles L. Jackson,
Samuel Cabot,
Henry B. Hill,
Leonard P. Kinnicutt.
Arthur M. Comey.

The President appointed the following Standing Committees: —

Committee of Publication.

CHARLES L. JACKSON, WILLIAM G. FARLOW,
CHARLES G. LORING.

Committee on the Library.

HENRY P. BOWDITCH, AMOS E. DOLBEAR,
EDWARD J. LOWELL.

Auditing Committee.

HENRY G. DENNY, JOHN C. ROPES.

On the motion of the Corresponding Secretary it was

Voted, That the thanks of the Academy be tendered to Wolcott Gibbs for his long and valuable services as member of the Rumford Committee.

The following papers were presented by title: —

On those Orthogonal Substitutions that are given by Cayley's Expression, or by the Limiting Form of Cayley's Expression. By Henry Taber.

On the Measurement of Resistance by the Method of Substitution. By G. Le Clear.

On the Currents in Batteries made up of Cells joined up in Multiple Arc. By B. O. Peirce.

On the Constitution of the Nitroparaffine Salts. Second Paper. By John U. Nef.

On Ternary Mixtures. First Paper: The Chemical Potential of Metals. By Wilder D. Bancroft.

Action of Alcoholates on Chloranil. By C. Loring Jackson and H. S. Grindley.

Bromine Derivatives of Metaphenylene Diamine. By C. Loring Jackson and S. Calvert.

Behavior of certain Derivatives of Benzol containing Halogens. By C. Loring Jackson and S. Calvert.

A Revision of the Atomic Weight of Strontium. First Paper: The Analysis of Strontic Bromide. By Theodore W. Richards.

On the Cupriammonium Double Salts. Second Paper. By Theodore W. Richards and A. H. Whitridge.

On the Cupriammonium Double Salts. Third Paper: Compounds of Iodine. By Theodore W. Richards and G. Oenslager.

On a Series of Cupraniline Compounds. By Theodore W. Richards and F. C. Moulton.

Euglenopsis, a new Alga-like Organism. By Bradley Moors Davis.

New Plants of Northwest Mexico, collected by Messrs. C. V. Hartman and C. G. Lloyd upon the Lumholtz Archæological Expedition. By B. L. Robinson and M. L. Fernald.

On the Cell Lineage of the Ascidian Egg. A Preliminary Notice. By W. E. Castle.

The North American Ceuthophili. By S. H. Scudder.

Researches on Electrical Waves. By John Trowbridge.

On the motion of the Corresponding Secretary, it was

Voted, That the Rumford Committee be directed to defray the cost of the publication of John Trowbridge's paper on "Electrical Waves" from the income of the Rumford Fund.

Eight hundred and sixty-eighth Meeting.

October 10, 1894. — STATED MEETING.

The VICE-PRESIDENT in the chair.

The Corresponding Secretary read the following letters: from the Scientific Alliance of New York, requesting the co-operation of the Academy in the endeavor to obtain a reduction of postage rates on natural history specimens; from the Royal Society of New South Wales, offering its medal and twenty-five pounds for the best communication containing the results of original researches on a series of specified topics; from the Imperial Russian Geographical Society, enclosing a copy of a pamphlet "Respecting the Necessity of an International Agreement with regard to the Publication of Material contained in Naval Meteorological Journals, a Memorandum drawn up by Rear Admiral Makaroff, St. Petersburg," and requesting the Academy to favor the Society with its views thereon; from the Royal Academy of Sciences of Turin, announcing the deaths of Commanders Frebretti and Lessona; and from H. von Holst, John Donnell Smith, and Ingram Bywater, acknowledging their election into the Academy.

The chair announced the death of Josiah Parsons Cooke, President of the Academy; of Oliver Wendell Holmes and Edward J. Lowell, Resident Fellows; of E. G. Robinson and W. D. Whitney, Associate Fellows, and of H. L. F. von Helmholtz, a Foreign Honorary Member.

The vacancy occasioned by the death of the President, Josiah Parsons Cooke, was filled by the unanimous election of

ALEXANDER AGASSIZ, *President.*

On motion of the Corresponding Secretary, it was

Voted, That the December meeting be devoted to addresses in memory of the late President of the Academy, Josiah Parsons Cooke.

Voted, To appropriate the sum of two hundred dollars ($200) from the income of the C. M. Warren Fund to Francis C. Phillips, of Allegheny, Pennsylvania, in aid of his researches relating to the Chemistry of Natural Gas; and six hundred dollars ($600) to Charles F. Mabery, of Cleveland, Ohio, in aid of his investigations of the Sulphur Petroleums.

The following report was adopted: —

The Committee, appointed at the Annual Meeting to consider the changes in the Statutes proposed by S. H. Scudder, and the amendment offered by H. P. Bowditch to the rule for the nomination of officers of the Academy, recommends the following alterations in the Statutes: —

Chapter II., Section 1, change the words "a Vice-President" to "three Vice-Presidents, one for each Class." Change the words "written votes" to "ballot."

Section 2, change the word "Vice-President" to "the three Vice-Presidents."

Section 3, add at the end, "or at a meeting called for this purpose."

After Chapter II. insert a new Chapter III., "Of Nominations of Officers," and alter the numbers of the following chapters to correspond to this change. The new chapter to read as follows: —

"CHAPTER III. — OF NOMINATIONS OF OFFICERS.

"1. At the stated meeting in March the President shall appoint from the next retiring Councillors a Nominating Committee of three Fellows, one for each Class.

"2. It shall be the duty of this Nominating Committee to prepare a list of candidates for the offices of President, Vice-Presidents, Corresponding Secretary, Recording Secretary, Treasurer, Librarian, Councillors, and the Standing Committees which are chosen by ballot; and to cause this list to be sent by mail to all the Resident Fellows of the Academy not later than four weeks before the Annual Meeting.

"3. Independent nominations for any office, signed by at least five Resident Fellows and received by the Recording Secretary not less than ten days before the Annual Meeting, shall be inserted in the call for the Annual Meeting, which shall then be issued not later than one week before that meeting.

"4. The Recording Secretary shall prepare for use in voting at the Annual Meeting a ballot containing the names of all persons nominated for office under the provisions given above.

"5. When an office is to be filled at any other time than at the Annual Meeting, the President shall appoint a Nominating Committee, in accordance with the provisions of Section 1, which shall announce its nomination in the manner prescribed in Section 2 at least two weeks before the time of election. Independent nominations, signed by at least five Resident Fellows, and received by the Recording Secretary not later than one week before the meeting for election, shall be inserted in the call for that meeting."

Chapter III. of the present Statutes, Section 1, change the word "Vice-President" to "Senior Vice-President present," and insert at the end of the section, "Length of continuous membership in the Academy shall determine the seniority of the Vice-Presidents."

C. L. JACKSON,
S. H. SCUDDER,
F. W. PUTNAM,
Committee.

The following report was presented and adopted: —

Report of the Committee to consider the Circular of the Royal Society in regard to a Catalogue of Scientific Publications.

The Committee finds itself fully in sympathy with the desire of the Royal Society to improve the methods of cataloguing scientific literature, and is distinctly of the opinion that the establishment of such a catalogue, to be compiled through international co-operation, is both desirable and practicable.

It seems probable that this improvement in the methods of cataloguing may best be made by establishing some form of card catalogue prepared by the co-operation of a central bureau with the various publishers and editors of scientific literature in issuing with each book and with each number of every periodical a set of cards of standard size and type, each card to exhibit for a book or for a single article in a periodical, —

1st. The name of the author.

2d. The title of the book or article.

3d. The date, place and house of publication of the book, or the title, volume, and page of the periodical, in which the article appears.

4th. A brief statement, not to exceed eight or ten lines, to be prepared by the author himself, setting forth the general purport of the book or article so as to furnish the necessary data for cross references.

Such cards should be in duplicate, to permit of arrangement according to subject or author, or both if desired, and additional cards should be issued whenever the character of the title necessitates cross references.

If thought desirable the type used in printing the cards could be kept set up till the end of the year, and then, by arranging the material according to subjects, an annual report in book form could readily be published.

A central bureau charged with the work as above outlined could very properly be established under the auspices of the Royal Society. In this central office subscriptions could be received from libraries and individuals for cards relating to the articles published in certain journals, or to the literature of certain departments of science, and a subscriber would thus receive, in weekly instalments, a complete card catalogue of all the literature in his own line of work.

The Committee present only a general outline of the plan for this card catalogue, as it is understood that the details of the scheme will be sent to the Committee of the Royal Society by Harvard University. They would further express the hope that some plan may be successfully inaugurated at an earlier date than the year 1900, as suggested in the circular of the Royal Society.

In accordance with the views above set forth the Committee respectfully recommends to the American Academy the adoption of the following votes: —

1. That, in the opinion of the American Academy of Arts and Sciences, the establishment of a catalogue of scientific literature to be maintained through international co-operation is both desirable and practicable.

2. That a copy of this report be transmitted to the Royal Society, as a suggestion of the way in which this plan may be best carried out.

3. That in case such a card catalogue as that recommended in this report be established, it is desirable that the American Academy co-operate with the central bureau by forwarding titles and summaries of the articles published in its Proceedings and Memoirs.

(Signed,)
C. L. Jackson,
H. P. Bowditch,
Denman W. Ross,
Committee.

The Corresponding Secretary read an abstract of C. F. Mabery's paper, "On the Composition of the Ohio and Canadian Petroleums."

The following papers were read by title: —

On the Electric Resistance of certain Poor Conductors. By B. O. Peirce.

On the Variability in the Spores of the Uredo Polypodii. By B. M. Duggar.

Note on the Effect of Temperature on Hysteresis. By Frank A. Laws and Henry E. Warren.

The Recording Secretary presented a copy of the Proceedings of the International Congress on Water Transportation, held at Chicago in 1893, and remarked that it contained a memoir on Electric Haulage which anticipated two papers presented this year at the International Inland Navigation Congress at the Hague, at which he was present.

Eight hundred and sixty-ninth Meeting.

November 23, 1894. — SPECIAL MEETING.

The Academy met at the house of the President, at Cambridge.

The PRESIDENT in the chair.

The death of Robert C. Winthrop, a Resident Fellow, was announced; also, the death of James McCosh, an Associate Fellow.

The President, after acknowledging his indebtedness to the Academy for the high honor conferred upon him by his election. proceeded to give an account of his explorations in 1891 in connection with the U. S. Fish Commission in the Steamer "Albatross," commanded by Captain Z. L. Tanner.

This expedition opened the deep water of the Panamic Region as far west as the Galapagos and as far north as the Gulf of California. He compared the deep water Panamic fauna with the abyssal fauna of the Caribbean, as well as the primal conditions of life existing in the ocean on the two sides of the Isthmus. When contrasting the coral fauna of the two seas he took occasion to refer to his recent explorations of the coral reefs of the Bahamas and of the Bermudas, and to indicate their bearing on the Darwinian theory of the formation of coral reefs. The exploration of the Bahamas took place in the spring of 1893, in the Steam Yacht "Wild Duck," owned by the Hon. John M. Forbes. That of the Bermudas was made in March, 1894.

Morrill Wyman read a paper entitled, "Experiments and Observations on the Summer Ventilation and Cooling of Hospitals."

The following papers were presented by title: —

Contributions from the Gray Herbarium of Harvard University. New Series, No. 9: A Revision of the North American Cruciferæ. By S. Watson and B. L. Robinson.

Experiments on the Relation of Hysteresis to Temperature. By Frank A. Laws and Henry E. Warren.

Notes on Laboulbeniaceæ, with Descriptions of New Species. By Roland Thaxter.

Eight hundred and seventieth Meeting.

December 12, 1894.

The PRESIDENT in the chair.

The President announced the death of Ferdinand Marie de Lesseps, Foreign Honorary Member.

On the recommendation of the Council, it was

Voted, That the use of the Academy's room be granted to the Colonial Society of Massachusetts on the third Wednesday afternoon of each of the five months December to April, in the same way as during the past year.

The meeting was devoted to a commemoration of the late Josiah Parsons Cooke, President of the Academy.

ADDRESS OF CHARLES LORING JACKSON.

JOSIAH PARSONS COOKE, for forty-one years a Resident Fellow of the Academy, Librarian for eight years, Corresponding Secretary from 1873 till 1892, and President in 1892, 1893, and 1894, was born in Boston on October 12, 1827, and died in Newport on September 3, 1894.

He was descended from Major Aaron Cooke, who came in 1630 to Dorchester, Massachusetts, from England, and afterward was one of the founders of Northampton, where he died in 1690. His son, also named Aaron, lived in Hadley, and it was under his protection that the regicides Goffe and Whalley lay in hiding in that town. Noah Cooke, the fifth in descent from Major Aaron Cooke, after serving as a chaplain in the war of the Revolution, moved to New Hampshire, where a son, Josiah Parsons Cooke, the father of the subject of this memoir, was born, in 1787. After a boyhood passed in Keene he graduated from Dartmouth College in 1807, and then established himself in Boston as a lawyer, where, in 1826, he married Mary Pratt, the eldest daughter of John Pratt, a well known merchant.

On October 12, 1827, a son was born, who was named Josiah Parsons Cooke after his father. In 1833 Mrs. Cooke died in Santa Cruz, and her little son, only six years old, and a younger sister, now Mrs. Bennett Hubbard Nash, were left to the devoted care of a faithful friend, who did all that was possible to replace the mother whom they had lost.

Young Cooke grew up a quiet boy, little given to sports out of doors, especially as early in his boyhood a course of lectures given in Boston by the elder Silliman kindled in him an enthusiasm for chemistry, which continued to blaze till the end of his life, and led him to pass all his spare time, not on the playground, but in a little laboratory which he had fitted up in his father's house. Here he attacked the science by experiment, guided by the bulky volume of Turner's Chemistry, and secured a mastery of the subject which would have been highly creditable with a good instructor, but without a teacher of any sort was most surprising. Yet, while a remarkably able student in chemistry and also in mathematics, he had neither taste nor aptitude for the dead languages, and it was only with much difficulty that he surmounted the barrier of Greek and Latin which guarded the approach to Harvard College.

Once fairly in College he distinguished himself in mathematics, but found little instruction in his favorite science. Professor Webster, then near the end of his service, gave the class two or three chemical lectures, which were brought to a sudden end by his show experiment called the volcano, — a large heap of sugar and potassic chlorate piled on a slab of soapstone. After he had lighted it with a drop of sulphuric acid, he saved himself by dodging out of the room, and in a very few seconds all the members of the class found themselves obliged to jump out of the windows. Later, Professor Horsford, who had just taken charge of the laboratory of the Lawrence Scientific School, to fill the gap gave a voluntary course of lectures on chemistry, which, however, did not extend beyond three, so that the teaching of chemistry which he received in Harvard College did not perceptibly add to his knowledge of the science acquired by his own exertions.

After his graduation, in 1848, a year was spent in European travel, and on his return, in the autumn of 1849, he was made Tutor in Mathematics at Harvard College; but the absence of all chemical teaching in the College soon gave him more congenial occupation, since a few weeks after his appointment he was asked to give instruction in chemistry to the Freshmen, and in the following spring (May 25 1850) was appointed Instructor in Chemistry and Mineralogy, with the following condition, — "he providing at his own charge the consumable materials necessary in performing chemical experiments." In this one does not know which to admire more, the liberality of the arrangement or the elegance of the language. The materials to be provided by him need not have been confined to those "consumable," however, since the College possessed no apparatus worth mentioning, and his two courses of lectures given in 1850 were illustrated by material brought from the small private laboratory which he had fitted up at home when a boy.

At the end of this year it was decided to fill the Erving Professorship of Chemistry and Mineralogy, and the two most prominent candidates were Cooke and David A. Wells, the first graduate in chemistry of the Lawrence Scientific School, now so eminent for his work in political economy. The election resulted in the choice of Cooke on December 30, 1850, and he held this position till his death. He was now only twenty-three years old, with barely a year and a half of experience as a teacher, and a knowledge of chemistry the product of his own studies unaided by any systematic instruction. With this meagre outfit he was confronted with problems which would have tasked the abilities of an old, experienced, and fully educated professor. The chemical teaching in Harvard College had become extinct, he must re-establish it. The College was wedded to methods of teaching excellent for classics and mathematics, but entirely unfit for a subject like chemistry; he must displace these, and put in their stead better methods, many of which were still to be invented. Finally, he must help to raise science from its position as an unwelcome interloper on the outskirts of the College course to an equality with the humanities intrenched behind centuries of tradition.

His first step after his appointment was to obtain leave of absence for the remainder of the College year, which was well spent in Europe buying apparatus and chemicals, mostly at his own expense, according to an agreement between the Professors of the Medical School; but he also found time to improve his intellectual equipment by attending the lectures of Regnault and Dumas, whose influence can be traced in his strong leaning to chemical physics, and the care and accuracy of his later work upon atomic weights. Regnault especially inspired him with the warmest affection, as is pleasantly shown by the enthusiastic reverence with which he is invariably mentioned in his book on Chemical Physics. With this work his systematic instruction in chemistry, if it can be called such, began and ended, and it is hard to believe in view of his achievements that it was all crowded into six months, broken by many other necessary occupations.

On his return from Europe in 1851 he promptly accomplished his first task, the re-establishment of chemical instruction in Harvard College on its old recitation basis; but it is a high tribute to his penetration and judgment that he recognized from the first the insufficiency of this way of teaching, and turned eagerly to the laboratory method, invented by Liebig not many years before, and brought to the Laboratory of the Lawrence Scientific School by Horsford, a pupil of Liebig, in 1847. The reason for this, Cooke tells us, was that he had taught himself chemistry by experiment. His second great task, the introduction of this laboratory method, proved no easy one. A beginning was made even in his first year of service as Erving Professor by fitting up a small laboratory in the north end of the cellar of University Hall, under the lecture and apparatus rooms assigned to the Chemical Department. Here Storer, Eliot, Dean, just home from Wöhler's laboratory, and many others, worked as volunteers, but it took seven years of hard fighting to get this course adopted by the College as anything but an extra. Meanwhile he was striving to improve the regular courses by introducing into the two weekly recitations Stöckhardt's Chemistry as the text-book, since this made a first though crude attempt to follow the experimental method of presenting the subject, and by laying great stress on writing reactions, which, to use his own words, "served its purpose in making the study respected in a literary community; but it did this at the sacrifice of all that is distinctive and peculiarly valuable in the study of an experimental science." This led to the publication of his first book, in 1857, which was a thin volume called "Chemical Problems and Reactions," an admirable manual of tactics for this recitation drill. Amid this arid desert of recitations the weekly lecture was the one green spot, as here experimental demonstrations were not only allowed, but required, and yet these lectures were surrounded by difficulties before which most men would have given up in despair. The apparatus which he had brought home from Europe was bought for the Medical School; but, as the College had no chemical collection, it was obliged to do double duty, and the frequent transportation from Cambridge to Boston and from Boston to Cambridge of these bulky and fragile pieces of apparatus used up much time and energy, and must have been a constant strain upon his nerves.

His duties at the Medical School, which at first divided his time with the College, were irksome in the extreme. Chemistry was systematically neglected by the students, and the fact that he held no medical degree caused a certain amount of friction with his colleagues, but nothing could damp his youthful enthusiasm, and laboratory courses in qualitative analysis and medical chemistry were established by him, although tolerated in the School only as extras. It was at this time that he prepared and delivered a long course of lectures on organic chemistry to satisfy a wholly unintelligent demand on the part of the medical students, to which he alludes later as a monument of useless labor; but this was not the case, as the familiarity thus gained with a field so different from that which he cultivated in after life had a most excellent effect in broadening his view of the science. It was a great relief to him when, in 1857, he was freed from his duties at the Medical School, the apparatus made its last journey over the bridge, and henceforward he was able to devote his time and energy to the development of the chemical department of Harvard College.

But it must not be inferred that during these early years all his attention was given to teaching, as his first scientific paper, that on the Classification of the Elements, dates from this period, since it was published in 1854. It created a marked sensation when, in December, 1853, he presented it to our Academy, to which he had been elected in the previous year. Benjamin Peirce in particular hailed it as a wonderful discovery, and this, as Cooke once told me, had a bad effect on his subsequent work for many years, both by keeping him from many excellent researches because they did not promise far-reaching theoretical results, and by making him try to find such results in all the work that he did. These tendencies unfortunately were not counteracted by association with other chemists, for, although he had many scientific acquaintances, he was singularly unwilling to discuss chemical subjects with them, owing, it would seem, to a natural sensitiveness and reticence inherited from his father, and not modified by study in one of the large foreign laboratories, where a man learns among other useful lessons that all scientific men are comrades. It took him twenty years to shake off this habit of mind, and to grow into a better and therefore more prolific mood in reference to research.

The year 1858 was a most important epoch in his life, as at this time the proper method of chemical instruction was recognized by the acceptance of the experimental course in qualitative analysis as a regular elective study in the College, and also satisfactory laboratory accommodations were provided by the erection of Boylston Hall.

In the ten years that followed no new courses were added, but that already established was perfected, and its success gradually accustomed the College authorities to the new method of instruction, and prepared them for the further advance at the end of this period. But although these years from 1858 to 1868 show no striking changes in the curriculum or very important papers, they are rich in literary activity. His first large book, the "Elements of Chemical Physics," was published in 1860, an excellent account of this branch of the science as it existed at that day, which ran through three editions, and was still used at Oxford within a very few years. At the very end of this period his second important text-book appeared, the "Chemical Philosophy," published in 1868 (four editions), a wonderfully clear and complete exposition of the modern theories of chemistry. Neither of these books was popular with the students. They could not be, as they obliged their readers to think, and there is no occupation more distasteful to the undergraduate. I can well remember the utter despair which settled upon me when I attacked my first problem in the Chemical Physics. I had never been called upon to think unassisted before, and at first I doubted the possibility of the process. But in this very demand on the thinking powers of the student lay the chief usefulness of these books, and their educational value on this account can hardly be overestimated. Nor would the fact that this work was distasteful have troubled him much, as he often expressed his disapprobation of the sugar-coating now so generally considered essential on educational pills.

A book of an entirely different sort came out between the two which I have just mentioned. This was "Religion and Chemistry, or Proofs of God's Plan in the Atmosphere and its Elements" (1864, and a new edition in 1880). It consisted of a course of lectures delivered before the Brooklyn Institute, the Lowell Institute of Boston, and the Mechanics' Association of Lowell, in 1861. In it the argument of natural theology is worked out in great detail from chemical data, and his stores of scientific knowledge are brought to the service of his sincere and earnest piety.

In 1860, he married Mary Hinckley Huntington, of Lowell, who survives him. Some years later Oliver W. Huntington and his sister (now Mrs. W. A. Pew, Jr.), a nephew and niece of Mrs. Cooke, became members of his family; and their presence did much to brighten his life, and gave additional objects for his warm affection.

For many years before 1868, the Catalogue had contained the following announcement: "Mineralogy is taught to those who desire to learn it by Professor Cooke." This was associated with a similar announcement about Hebrew, and the number who desired either of these incongruous companions was small. Enough however studied mineralogy to prove to Cooke, "somewhat to his own surprise, that, when made solely a subject for object lessons, the study of determinative mineralogy was an admirable training of the powers of observation, and therefore a disciplinary study of the highest value." Accordingly a certain amount of mineralogy was crowded into the single chemical elective, and when, in 1868, a second elective was introduced, this was devoted entirely to that subject, leaving all the time of the original course for qualitative analysis.

After this time there was a continual increase in the number of the chemical courses, until, in 1871, the single laboratory of the original building became overcrowded, and new accommodations were secured by adding to Boylston Hall a story, which contained a large laboratory for elementary students. At about the same time the chemical department of the Lawrence Scientific School was merged in that of the College, and all the chemical material was removed from the Scientific School building to Boylston Hall. Cooke had now essentially accomplished the three tasks which confronted him when appointed Erving Professor. Chemical teaching was established in the College; the new methods of instruction had been introduced; and equal rights for science had been gained after a hard struggle in the Faculty, in which Cooke took a prominent part, and showed rare powers as a debater and a strategist. It only remained for him to gather the fruits of the victory.

In 1872 he was elected a member of the National Academy of Sciences. In 1873 he was made Corresponding Secretary of our Academy, and for twenty years after this he managed our correspondence and publications, and to him is due the establishment of an annual volume of the Proceedings.

Of the many courses of popular lectures which he gave at this time, one delivered before the Lowell Institute of Boston was embodied in a book called "The New Chemistry" (1874), containing a clear popular account of the modern chemical theories, which he had already treated in a more technical way in his Chemical Philosophy. This book had a striking success. It ran through five editions in English in four years, and was translated into nearly all the civilized languages of the globe. It still remains one of the best and most readable statements of the theories of chemistry.

In 1876 he was elected an Honorary Member of the London Chemical Society, and a few years later a Member of the Royal Institution.

One of his principal amusements was photography, in which he attained remarkable skill, and not only did he take excellent photographs himself, but he collected an enormous number of photographic slides, and his frequent exhibitions of these to his friends or his classes were most enjoyable, the beauty of the views being enhanced by his vivid descriptions and comments. His own pleasure in these exhibitions must have been as great as that of his audiences, since he was never tired of giving them, in spite of the very considerable amount of trouble and labor which they involved.

The manifold employments which I have tried to sketch left Cooke little time for original investigation, and this, combined with the too exaggerated conception of the dignity of research which he had formed in early life, as I have already said, prevented him from publishing before 1874 very many or very important papers, if we except his discoveries of minerals in Rockport. All this time, however, his chemical ability and insight were slowly ripening, and in 1874 the harvest began with his paper on the Vermiculites, which was closely followed by his researches on Antimony and on Oxygen, so that from this time till 1889 his scientific production was continuous and important.

This scientific activity did not interfere with his other occupations. During this period the number of chemical electives was increased, new laboratories were fitted up, and the growth of the Mineral Cabinet was incessant. This collection of minerals was an object of such affectionate care to him that no account of his life would be complete without a sketch of its history. Starting in comparative insignificance both in quantity and quality at the time he was made Professor, it grew at first slowly, principally by the collections which he made in vacation excursions, and by occasional purchases, until during one of his earlier journeys to Europe he succeeded in buying the collection of Count Liebener, rich in uncommon minerals from the Tyrol. After this it increased steadily by quiet purchases, often paid for out of his own pocket, until in 1875 it crowded Comparative Anatomy, which originally shared Boylston Hall with Chemistry, into other quarters; but in 1891 Mineralogy in its turn had to yield to Chemistry, which was left in undisputed possession of the whole building. To provide new quarters for the minerals, a division of the University Museum was built largely through his exertions, and here the collection was installed, which in the mean time had risen to be one of the first in the world so far as meteorites are concerned by the addition of the J. Lawrence Smith collection, partly left to the College by its original owner, and partly bought with money raised or subscribed by Professor Cooke. Since then the generous gifts of Mr. J. A. Garland of New York and Dr. W. S. Bigelow of Boston have given the collection a similar commanding position in regard to precious stones.

In 1877 he was made an associate editor of the American Journal of Science, and contributed to it then and afterward several excellent reviews of important papers.

In 1881 he collected a number of his essays and addresses in an interesting little volume entitled "Scientific Culture and other Essays." The address which gives its name to the book, and the two which follow, "The Nobility of Knowledge," and "The Elementary Teaching of Physical Science," display the penetrating insight and good judgment which he brought to bear on the problems of education; they are full of wise advice and inspiration. The book also contains appreciative biographical notices of Graham and W. H. Miller, and a paper on the radiometer, dwelling on the scientific principles brought out by this instrument. The careful and enthusiastic study of the radiometer, which led to this article, is exceedingly characteristic of the man. Whenever a striking new discovery was announced, he at once threw himself into the study of it with the greatest ardor. Thus he was probably the first to take calotypes in America, and later became an expert photographer, as I have already said. Shortly after Bunsen and Kirchhoff's great invention, he constructed the most powerful spectroscope of that time, inventing many ingenious contrivances for making the necessary adjustments; several of his papers owe their origin to this work on spectrum analysis, and he was on the point of making a discovery of the first order, the method of seeing the solar prominences in spite of the full glare of the sun, when he was anticipated by two other observers. In the same way he mastered the new science of electrical measurements, procured the necessary apparatus, gave instruction in this subject to voluntary students, and wrote a popular account of its principles.

In 1880 his father died, at a great age, and in the following year, after the graduation of his nephew O. W. Huntington from Harvard College, he went to Europe with his family, and passed the winter in Egypt. This was the last and longest of his many foreign journeys, and was rendered more noteworthy by the fact that on his return to England in the summer of 1882 the University of Cambridge conferred on him the honorary degree of Doctor of Laws.

In 1887 he returned to the field of Natural Theology in a course of lectures before the Union Theological Seminary of New York, which was repeated before the Lowell Institute of Boston, and published in 1888 under the title, "The Credentials of Science the Warrant of Faith." This book, which has passed through two editions, was intended for students of divinity, and the argument therefore is more technical than that in "Religion and Chemistry." It consists in proving the thesis "that the inductions of natural theology are as legitimate as the inductions of physical science." The illustrations are drawn from astronomy and physics quite as often as from chemistry, and the strong metaphysical bent of his mind is very apparent. Like all of his books which are not text-books, this one shows that he was a devoted and appreciative student of Tennyson, "in whose verses," he says, "he has discovered a truer appreciation of the difficulties which beset" the relation of science and religion "than he has ever found in the philosophy of the schools."

In 1889 he received the degree of Doctor of Laws from Harvard University; and now began the melancholy period when failing health interfered with, though it could not stop, his various activity and wonderful industry. Through it all he was supported by the devoted help and affection of his wife's nephew, O. W. Huntington, who, as he often said, was in every respect the staff of his old age.

A severe functional trouble, which would have thrown most men into retirement, and a serious affection of his eyes resulting in the loss of one of them, were unable to overcome his persistent energy. It is true that he was obliged gradually to abandon his own original work, but he still directed that of a few advanced students, and gave several courses of instruction, including the lectures on general chemistry, to the whole Freshman Class, a labor which would tax severely the powers of a young and sound man. These lectures had continued, with only occasional breaks of not more than two years at a time, ever since he began teaching chemistry in 1850. In the latter years of his life they ceased to be a systematic course in chemistry, and became rather an inspiring statement of the methods, aims, and needs of the science, thus admirably serving their purpose by awakening an enthusiasm for scientific work among the students in their first year. The attendance on these later lectures was voluntary, and it was astonishing to see the crowd packed in the aisles of the old lecture-room, filling the vacant space before the table, and even extending well out into the entry, often with men standing on the stair-rail, and peering over the heads of those in front. As a college lecturer his style was striking and luminous, and his experiments uniformly successful, in spite of his tremulous hand, which one would have thought must have precluded any delicate manipulations. He has enriched the stock of lecture apparatus with many excellent contrivances, notably his arrangement for the projection of spectra, his form of the lecture-table eudiometer, and his vertical lantern. In the laboratory his explanations were clear and patient, and he always bore in mind the necessity of making the student think for himself. His students, whether elementary or advanced, regarded him with a warm affection, which was well merited by his exceeding kindliness, and his devotion to their interests.

In addition to these labors as a teacher he continued to serve as Director of the Laboratory, and even published an eighth book, "Laboratory Practice" (1891), a series of experiments to be used in fitting students for Harvard College, and in the corresponding College elective study, a course which he had founded, and in which he took till the end the strongest interest.

In 1892 he was elected President of our Academy, but in spite of a journey to Alaska, which gave him much needed change and recreation, he did not survive long to enjoy this well deserved honor. In the summer of 1894, after a most harassing winter, he went to his country house in Newport, where he had passed the summers for more than twenty years, and as soon as the strain of the term's work was removed broke down almost completely. Nevertheless, he managed to make out the European order for laboratory material for the following year in the midst of pitiable weakness, and then slowly, but without pause, faded away, until he died, on September 3, 1894.

ADDRESS OF HENRY BARKER HILL.

The scientific work of Professor Cooke began soon after his appointment to the Erving Professorship, and continued throughout his life. At first he seems to have been drawn toward subjects which were more or less intimately connected with mineralogy, his favorite pursuit, but in later years he turned to problems which tax to the utmost the patience and ingenuity of the investigator, and devoted the last half of his scientific life to the determination of atomic weights.

Forty one years ago, in December, 1853, he presented to the Academy a preliminary sketch of an investigation into the numerical relation of the atomic weights, and the Memoir upon this subject which appeared a few months later is noteworthy in that it was one of the early attempts to classify the elements through their atomic weights. It is, however, to us especially interesting in that it contained a discussion of the errors involved in the determination of atomic weights, which in a way foreshadows the investigations which occupied him in after life. The conclusions which he reached in this early paper Professor Cooke was able to quote thirty years later as the expression of his riper judgment.

An investigation upon the alloys of zinc and antimony, which followed soon after, in 1854, proved the existence of two definite crystalline compounds of the two metals. A subsequent study showed that the crystalline form of these bodies remained constant with a tolerably wide variation in percentage composition. This fact led him at the time to suggest that perturbation of the law of definite proportion could be effected by mass, and that these perturbations became serious wherever chemical affinity was weak. Six years later he applied the same course of reasoning to the composition of minerals, and came to the conclusion that the general formula in this case was but the typical formula toward which the mineral tended, but which perhaps was never realized with any actual specimen. Twenty-five years afterwards, when Butlerow again discussed the possible variability of the law of definite proportion, Professor Cooke, after referring to his own earlier views upon the subject, wrote that he felt the weight of evidence to be in favor of the atomic theory, and that absolute definiteness of combining proportion which this theory involves.

In 1860 appeared the detailed account of the brilliant researches of Kirchhoff and Bunsen upon spectrum analysis; and with characteristic enthusiasm Professor Cooke was soon absorbed in the study of this new mode of chemical investigation. Several papers appeared upon the construction of spectroscopes, the projection of the spectra of the metals, and upon the aqueous lines of the solar spectrum. While thus engaged in the study of the spectroscope, he found time to make a crystallographic examination of the acid tartrates of caesium and rubidium and of childrenite, and to investigate the dimorphism of arsenic, antimony, and zinc. The results of these investigations were published from time to time in the American Journal of Science.

For several successive years he was now engaged in the study of new mineral species. In 1866 he described danalite from Rockport, Massachusetts, and in the following year cryophyllite from the same locality. He also described at this time two analytical processes which had evidently been suggested by his work upon these minerals. A few years later appeared a paper upon the vermiculites, in which two new species or varieties, hallite and culsageeite, were described, and this was supplemented in the following year by an account of the investigation, with F. A. Gooch, of two more varieties of the same family. These researches, together with a note upon melanosiderite and a crystallographic study of some American chlorites, were the last of his purely mineralogical contributions.

Before the publication of these papers upon the vermiculites, Professor Cooke had begun the study of antimony, and was able to present to the Academy, in June, 1873, a preliminary notice of some determinations of its atomic weight. So many difficulties were encountered, however, that the extended paper upon the subject did not make its appearance until four years later. In 1854 he had expressed the opinion that the accidental errors affecting such determinations could easily be eliminated, while the constant errors were the great errors involved. In 1877 he closes the account of his revision of the atomic weight of antimony with the remark that the investigation from the first had been a study of constant errors. It is not possible to tell briefly the story of the persevering search for these constant errors, — a search involving months of patient labor. I could but repeat the words with which Professor Cooke has himself described, with painstaking fidelity, the steps which he took in surmounting the successive difficulties. The hardest task, possibly, was to show the constant error which vitiated the results obtained by Dumas twenty years before, — results which had been wellnigh universally accepted.

The careful study of the compounds of antimony with the halogens, which was a necessary preliminary to the determination of its atomic weight, established many interesting facts, the most important of which, possibly, was the existence of three different crystalline forms of antimonious iodide belonging, respectively, to the monoclinic, orthorhombic, and hexagonal systems. The results of the quantitative study of antimonious bromide, confirming the value of the atomic weight of antimony which he had previously established, were given in a paper which appeared a year or two later, and the advantage which could be gained by the simultaneous determination of three atomic ratios was here discussed. The evidence was now complete, and the new atomic weight of antimony was adopted by the whole chemical world. A series of less important papers appeared during the progress of this work upon antimony, describing new methods devised for the work, or discussing details of the processes involved. Among them may be mentioned "A new method for manipulating hydric sulphide," "The process of reverse filtering," "Argento antimonious tartrate," and "The solubility of chloride of silver in water."

Shortly after the completion of the work upon antimony, Professor Cooke planned an investigation upon the relative values of the atomic weights of oxygen and hydrogen. The necessary exploratory work upon this research was delayed by failing sight and precarious health, so that it was not until the autumn of 1886 that everything was ready for the final decisive experiments. During the following winter, with the co-operation of T. W. Richards, numerous determinations were made, in which an accurately weighed quantity of hydrogen was burned, and the weight of water which was formed determined. The experimental difficulties involved were great although they were in kind quite different from those which the work upon antimony presented. These difficulties were at last overcome, and the wonderfully close agreement between sixteen successive determinations, made with hydrogen prepared in three different ways, showed how perfectly all sources of accidental error had been eliminated.

One source of constant error had been overlooked, however, which affected not only these determinations but all the results which had ever been obtained by the classic method of Regnault. Agamennone, and afterward Lord Rayleigh, discovered that the volume of a glass vessel was sensibly diminished when the air within it was exhausted, so that the tare of the globe in which the hydrogen had been weighed had been incorrectly determined on account of the diminished volume of the air displaced. The amount of this error could easily be determined, and in a second paper the necessary small correction was applied. In order to avoid this change of volume, he devised an ingenious method for determining the tare of the globe without exhausting it; and this method was the subject of his last communication to the Academy, in June, 1889.

As an investigator Professor Cooke was clear in thought, persevering amid difficulties, fertile in expedients. impatient of dogma, and to the end he retained the keen curiosity and enthusiasm of his earlier days.

ADDRESS OF AUGUSTUS LOWELL.

It is always interesting to trace the impulse which had determined a man's life work. It is peculiarly so to me in the case of Professor Cooke, because he himself was wont to attribute it in a large measure to the impression made upon him as a boy by the lectures of Professor Silliman, before the Lowell Institute. These lectures opened a new horizon. He was intensely interested, repeating the experiments he had witnessed with such imperfect appliances as he was able to procure, and from that moment there was no hesitation as to his future. His life was to be devoted to the study of Chemistry.

There was nothing in his birth or surroundings to indicate such a career. His father was a successful lawyer; his maternal ancestors devoted to commerce. The pursuit of Science for its own sake was little understood or appreciated. There was no adequate teaching, and those of us who can remember the lectures in Holden Chapel will realize what must have been the difficulties of a young beginner.

When the College lost its Professor of Chemistry, it was not easy to fill the position. The same necessity which had called a young Divinity student to the Professorship of Physics, placed an untried youth in the chair of Chemistry. The choice was justified, however, by the result.

To a keen mind and power of analysis Cooke added a gift of language and clearness of statement which made him a natural lecturer. It was said of him that he recalled the manner of Faraday; and whether he was explaining the mysteries of Science, describing the recently discovered Pharaohs, or treating of the higher issues of religious thought, the same charm marked his discourse. With uncertain muscles which often seemed to imperil the success of an experiment, there was no hesitancy in thought or utterance. All was clear, logical, and convincing. I never had the opportunity of hearing him at Cambridge, but I have often listened to his public lectures, and can bear witness that few lecturers held the attention of their audiences more completely than he, or gave more pleasure.

Professor Cooke did not confine himself to one subject of thought. He was many-sided. His religious lectures were marked by the same cogency of reasoning, purity of style, and apt illustration as any of his scientific discourses.

Professor Cooke lectured eight times before the Lowell Institute, and I cannot better indicate the breadth of his studies than by enumerating the subjects of these lectures.

In 1855 and 1856 he lectured on "The Chemistry of the Non-metallic Elements."

In 1860 and 1861, on "The Chemistry of the Atmosphere as illustrating the Wisdom, Power, and Goodness of God."

In 1864 and 1865, on "The Sunbeam, its Nature and Power."

In 1868 and 1869, on "Electricity."

In 1872 and 1873, on "The New Chemistry."

In 1878 and 1879, on "Crystals, and their Optical Relations."

In 1887 and 1888, on "The necessary Limitation of Scientific Thought."

In 1892 and 1893, on "Photographic Sketches of Egypt."

This last course recalled his travels and embodied the study and reflections of a cultivated mind amidst the monuments of that wonderful country. To it he brought the same patient investigation and broad generalization which marked his work elsewhere, and his treatment of it before his audience was generous, persuasive, and attractive.

One word I may be permitted in regard to his personal qualities. Professor Cooke was eminently simple, truthful, and earnest, kindly and affectionate. Possibly my connection with the Institute, which had done so much to determine his career and before which he had so often appeared, may have influenced his feeling, but to me he was always a kind friend, for whose attainments I had the highest respect, and whose pure, honest, confiding nature was always attractive and inspiring.

ADDRESS OF FRANCIS HUMPHREYS STORER.

I HAVE heard Professor Cooke say jokingly, but with a tinge of honest pride, that he was a "self-made chemist." The remark was true in one sense, for beside listening as a boy to a few popular lectures by the elder Silliman, and following for a brief period some of the public lectures of Dumas and other Parisians, he never had any definite, stated instruction in Chemistry. To the best of my knowledge and belief, he never worked for an hour in any other laboratory than his own. Many of the most familiar details of analytical manipulation he learned from his assistants while teaching them and his classes what Chemistry really is. It was from books and from his own inner consciousness that chemical knowledge came to him. Yet, thanks to native ability, to an excellent academic training, to inherited wealth, a clear head and a tenacious will, he came at last to stand in the fore-front of American chemists, and to command the attention of the fraternity in every land. Even as a manipulator, he became expert; in spite of a constitutional tremulousness, which, in his youth at least, had placed him at a great disadvantage. Like the surgeon with his knife, in the story, he had so mastered his trembling hand, that the thing held in it should shake assuredly into the right place.

But, although it is fair enough to say that as a chemist Cooke was self-taught, no such statement would be true of him as a scholar. There can, I think, be no question that a great part of the strength of the man depended upon a scholarship distinctly superior to that of most contemporaneous chemists. In point of fact, Professor Cooke was very carefully trained at College, where he came under the influence of many eminent men. Thanks to the teachings of Benjamin Peirce and Joseph Lovering, he became accomplished in the mathematics and in physics. Doctor Beck taught him Latin enough for his purposes. Felton and Sophocles strove with him as to Greek, and with Doctor Walker his relations were peculiarly intimate. He long continued to look up to President Walker as to a counsellor and guide. In the matter of rhetoric, he had the inestimable advantage of Professor Channing's drill. He was in contact also, to a certain extent, with such teachers as Asa Gray, Jeffries Wyman, and Longfellow. Incidentally, he obtained a good working knowledge of French and German.

It was by his mathematical studies more particularly that Cooke acquired that habit of thinking clearly and reasoning closely which distinguished him through life. To his academic training I attribute also much of that power of stating his thoughts clearly and forcibly, which made him one of the best teachers of his time. No matter what objection a purely literary person may be moved to urge against the use of the word "scholarship" as here applied, or what criticisms may occur to any one as to the style or manner of the man, it will still remain true that Professor Cooke's knowledge was ample and assured. In many respects it was profound! His reasoning was always cogent and his language plain.

I remember well the very favorable impression made by an address which he delivered at the opening of the Harvard Medical School, immediately after his appointment to a chair at that institution. There had been murmurings in the land that one so young and so inexperienced should have received the appointment. But they were silenced then and there, absolutely and forever.

There is, indeed, a certain note of distinction in many of Cooke's writings, such as is all too rare in scientific literature. Several of his memoirs might well be set before the laboratory student as models of clear presentation of a subject, in the same sense that, at an earlier time, we turned for such illustration to the writings of Gay-Lussac and Thénard, of Dumas, Boussingault, and Berzelius.

On looking beyond this immediate locality or centre, it will be seen that there have been thus far, here in America, four great chemical teachers; the elder Silliman, Hare at Philadelphia, Draper in New York, and Cooke at Cambridge; and of these four Cooke undoubtedly deserves to be placed first and foremost, in view of the fact that working and teaching chemists, trained by him, are scattered throughout the land. Were it not for this circumstance, it might perhaps justly be claimed that Draper's name should take precedence, because of the great influence he exerted during many years as a lecturer, a writer, and an investigator.

After all has been said, however, as to talent innate, power inherited, or wisdom acquired, it must still be remembered of our lamented President that he ranked higher than most men, because of the indisputable fact, that occasionally — at not infrequent times and seasons — his mind was illumined by divine sparks and flashes of genius.

ADDRESS OF CHARLES WILLIAM ELIOT.

Last spring an inquirer into the Department of Chemistry and Mineralogy in Harvard University would have found a building called Boylston Hall, one hundred and twenty feet by seventy, and three stories in height, completely occupied with the laboratories, store-rooms, and lecture-rooms for Chemistry, and a large section of the University Museum devoted to mineralogical collections and laboratories. Turning to the College Catalogue he would have found a series of elective courses in Chemistry, beginning with General Chemistry and Elementary Mineralogy, and rising through Qualitative Analysis, Quantitative Analysis, Organic Chemistry, Crystallography and the Physics of Crystals, Chemical Physics, and the Philosophy of Chemistry, to original investigation in various branches of both Inorganic and Organic Chemistry. Last year there were three hundred and fifteen choices of these courses made by graduate and undergraduate students; so that this number of places had to be provided in the laboratories of the department. The inquirer would also have seen large illustrative collections of apparatus, chemicals, and minerals, — and particularly the mineral collection would have struck him as extensive, well selected, and valuable. He would have found as teachers in the department three full professors, three instructors, and eight assistants. This elaborate and well equipped department of instruction has grown up in the course of forty-four years under the direction of one man, Josiah Parsons Cooke. I shall endeavor to show in some detail the strenuous, persevering, and well-directed labor by which Professor Cooke developed this admirable instrument of instruction and research. I might simply say in eleven words, — Professor Cooke created the Chemical and Mineralogical Department of Harvard University; but I should like to put before you some faint picture of the intelligence, energy, persistence, and enthusiasm which went into the accomplishment of that task. Mr. Cooke took the degree of Bachelor of Arts in 1848, but when he was an undergraduate at Harvard no Chemistry was taught there. I have often heard him say that he got his best guidance and incitement towards chemical study from the lectures of Professor Benjamin Silliman, the elder, before the Lowell Institute, in the early days of that invaluable institution. Although he had never received any systematic instruction in either Chemistry or Mineralogy, Mr. Cooke had acquired a considerable knowledge of the elements of both these subjects by 1849, and what is more, he had determined to be a teacher and a man of science. On the 3d of July, 1849, he was appointed Tutor in Mathematics in Harvard College, at the usual salary of $645 a year. Such an appointment seems almost incredible to the present generation, for he cannot be said to have received any professional training in Mathematics. In his view it merely offered an entrance into the Faculty of Harvard College.

On the 24th of November following, "Mr. Tutor Cooke was appointed (by the Corporation) to teach Chemistry to the Freshman Class next term. For this service, and for the apparatus and materials he may use, Mr. Cooke shall be paid $225." Such was the vote of the Corporation. The edge of the wedge was very thin; but it made a sufficient entrance. At the same meeting the Corporation voted, "As instruction in Chemistry for the undergraduates is no longer to be required of the Erving Professor (J. W. Webster), *Voted*, That for the rest of his services his salary be $1,000." Professor Webster's salary from the College (he was Professor also in the Medical School) had previously been $1,200. The Corporation had therefore taken $200 from his salary and given it to Mr. Cooke. It was an extraordinary coincidence that on the day before this ominous vote was passed Dr. Webster had killed Dr. Parkman; and on the 30th of November he was arrested for the crime. . . . During the ensuing term Mr. Cooke gave lectures to the Freshman Class, and held recitations; and then and there I, for one, first learned what Chemistry was about, and what was the scientific method in observing and reasoning.

On the 25th of May, 1850, the Corporation voted, "That Mr. Tutor Cooke, for the ensuing academic year, teach Mathematics to the Freshman Class, and Chemistry to the Sophomore and Freshman Classes, and Mineralogy to the Seniors, and that his salary shall be $1,000, he providing at his own charge the consumable materials necessary in performing chemical experiments." The frugality and prudence of the Corporation appear in these money votes. They had no idea of taking any great risk on the cost of illustrative materials;

but Mr. Cooke was fortunately indifferent on that subject. He had resources which enabled him to provide all necessary furniture, apparatus, and materials; and he used these resources with liberal good sense. He got possession in this first year of the lower northern lecture room in University Hall, and of a room about twenty by twenty-five feet in area in the northwestern corner of the basement of the same hall. There he fitted up the only chemical laboratory on the premises of Harvard College. There was already a good laboratory across Kirkland Street, in the new building of the Lawrence Scientific School; but with that the College had nothing to do. There was neither gas nor running water in University Hall, and Mr. Cooke's nearest neighbor on the adjoining corner of the basement was a baker's oven, where considerable batches of bread were baked every morning and every evening, and yeast was sold every afternoon. A pump in the cellar yielded water for both bakery and laboratory, and within fifty feet of the pump was a privy which served for the whole College.

On the 10th of July, 1850, Professor Webster's resignation was accepted. The young tutor had completed his plans for the ensuing year; but, for some reason which cannot now be determined, he procured a vote of the Corporation to settle one part of his plan. On the 31st of August, 1850, the President and Fellows voted, "That Stöckhardt's Principles of Chemistry be adopted as a text-book in the College." I know of no other instance within the last fifty years in which the President and Fellows have passed a vote concerning the adoption of a text-book.

On the 30th of December, 1850, Mr. Cooke was elected Erving Professor of Chemistry and Mineralogy, at the age of twenty-three. He had already demonstrated to the satisfaction of the Corporation that he was an efficient and prudent manager in business details, an interesting lecturer, and a zealous and singleminded College official. His salary was fixed at $1,200, "he paying all the expenses of his lectures, excepting that of fuel in Cambridge, the salary to commence on the first of March next." Again, a frugal arrangement which did not in the least discourage the youthful professor.

The vote describing his duties is an interesting one, for it illustrates the extraordinary expectation which it was then held reasonable to entertain concerning the teaching capacities of a youth of twenty-three: —

"*Voted*, that he shall reside in Cambridge, and be a member of the College Faculty, and that he shall give the lectures in the Medical College in Boston, and all the instruction required in Chemistry, Mineralogy, and Geology to the undergraduates, and perform such other duties as may from time to time be assigned him by the Corporation not inconsistent with the duties of the office."

Professor Cooke immediately resigned his Tutorship in Mathematics. He had now obtained the firm position from which he proposed to carry on the long campaign for the introduction of Chemistry and Mineralogy into the teaching of Harvard College. He held a permanent professorship; he was a member of the College Faculty, which his predecessor had never been, and he had established a small chemical laboratory in the middle of the College Yard. He prevailed on the Faculty to announce Chemistry for Freshmen in the second term of the year 1850–51, and Chemistry for Sophomores in the first term of the year 1851–52; also lectures on Mineralogy to Seniors in the first term of 1851–52. The introduction of these new subjects into a prescribed curriculum, which was already overloaded, is a subject for wonder and admiration. The present generation of teachers finds it hard enough to get new elective courses announced; but Professor Cooke successfully invaded a prescribed course in which the traditional subjects had long been securely intrenched.

In the second story of Harvard Hall was a large, miscellaneous, and unassorted collection of minerals and fossils, with some curiosities, which had been accumulating for years, but had received little care. Within a few months of his appointment as professor, Mr. Cooke made a survey of this inchoate collection. His knowledge of minerals was mathematical and physical rather than chemical, and he had no considerable experience in recognizing and determining them. He did not feel competent, without assistance, to sort the collection, and decide what to keep and what to throw away. He feared lest, through ignorance, he might reject valuable specimens; yet the sorting of the collection was obviously the first thing to be done. Under these circumstances he did a conscientious and courageous thing which, in my judgment, very few persons in his situation would have done. He employed Professor Benjamin Silliman, Jr., of Yale College, to sort the collection, and advise him what to keep and what to throw away. Professor Silliman performed this task with promptness and discretion, and the specimens then selected for preservation, — which naturally represented in the main the commoner species — constituted the skeleton, as it were, of the rich and ample collection of to-day. Out of this intercourse between Professor Silliman and Professor Cooke there grew a life-long friendship. The collection remained in Harvard Hall for eight years, being enlarged every year by Professor Cooke's constant activity in buying and collecting.

The Corporation soon found that it was difficult to resist the frequent demands of the young Professor. On the 25th of January, 1851, they granted "$200 to Professor Cooke for purchasing chemical apparatus for the laboratory at Cambridge for the use of the undergraduates." Observe the phrase, "the laboratory at Cambridge." It was still that little room in the basement of University Hall. On November 8th, 1851, by vote of the Corporation, Professor Cooke was "made a member of the Faculty of the Scientific School to teach Mineralogy to such students as may desire his instruction." His membership of the Scientific Faculty was always for Professor Cooke rather a security against the invasion of his precincts, than a means of prosecuting any aggressive campaign on his own part. For ten years there stood a notice in the Catalogue under the head of the Lawrence Scientific School to the effect that Professor Cooke would receive students in Mineralogy at his laboratory during the second term. Then for ten years more an enlarged notice under the same head invited scientific students to attend the course in Crystallography and Mineralogy which he was really providing for College students. In 1871–72, when the Scientific School was reorganized, all special mention of these opportunities was withdrawn.

The very next month — that is, in December, 1851 — the Corporation received a communication from the Erving Professor, "respecting the accommodation at present afforded for the chemical apparatus of the College." This communication was referred to President Sparks and Dr. Walker, two firm friends of Professor Cooke. The result was that he got possession of a room on the first floor of University Hall adjoining his lecture-room; and this room he immediately fitted up at his own expense with counters and other conveniences. He also got rid of the baker and occupied his quarters. On the 31st of January, 1852, the "Treasurer was authorized to discharge the account of Professor Cooke for apparatus in Chemistry and Geology procured by him in Europe for a sum not exceeding $150, in addition to the appropriation heretofore made for that purpose." In the following month they voted "that the Treasurer be authorized to expend a sum not exceeding $120, for the fitting up of the Rumford apparatus room." This was the room of which Professor Cooke had just got possession. In the mean time Professor Cooke had persuaded the Faculty to permit him to give lectures on Mineralogy to Juniors in the second term, and a course of lectures on Chemistry to Sophomores in the first term, — these in addition to the recitations in Stöckhardt's Chemistry in the second term for Freshmen, and in the first term for Sophomores. This was no inconsiderable amount of teaching for an inexperienced young man who had on his hands also the giving of a course of lectures at the Medical School in Boston, from the 1st of November to the 1st of March. At the building in North Grove Street, where he found plenty of space, and very little else, Professor Cooke fitted up an excellent laboratory for lecture purposes and for research. The Medical Class was turbulent, and always contained a considerable proportion of rough, uneducated young men; but the young professor made his lectures so interesting by carefully prepared experiments, that he rarely had trouble with his boisterous auditors. To the methods and policy of the Medical Faculty, on the other hand, he soon began to manifest a dislike, which before long became acute.

On the 26th of June, 1852, the President and Fellows passed a vote making "an *annual* grant of $200, half for minerals and half for chemical apparatus, to be disbursed under the direction of the Erving Professor, who will account for the same at the end of each academic year." That vote remains in force to this day; but the annual grant has risen from $200 a year to $800. It gave Professor Cooke something on which he could depend every year for the increase of apparatus and of the mineral collection.

In the following November, the Treasurer of the College laid before the Corporation "a catalogue of the Rumford and other apparatus belonging to the College, in charge of the Erving Professor of Chemistry, which had been examined and verified by him and found to be in good order." In less than two years Professor Cooke established his reputation with the Corporation as a trustworthy custodian of apparatus and other College property. This reputation stood him in good stead throughout his career. He had also secured laboratories both in Cambridge and Boston, procured considerable quantities of fittings and apparatus, and pushed his subjects into the prescribed curriculum of the College.

Let us turn now to consider what he did next in the Faculty. In 1852–53, he introduced a course of lectures on Chemistry, twice a week, for Seniors in the second term. He had already got access to the Freshmen, Sophomores, and Juniors. In the following year he gave up the Freshman Chemistry in the second term, in order to occupy both terms of the Sophomore year. The Senior lectures on Mineralogy disappeared, but instead, notice was given that Mineralogy is taught to those who desire to learn it by Professor Cooke. Considering that not a particle of Chemistry was taught to undergraduates, in 1850, he had certainly obtained a good position for his subjects in the College course by 1853. At the beginning of the medical term in the autumn of 1853, he was ready to receive a small number of medical students into his Boston laboratory, to pursue the subject of qualitative analysis, and James C. White, subsequently adjunct Professor of Chemistry in the Medical School, was a member of this first class. It is believed that this was the beginning in the United States of laboratory instruction in Chemistry for medical students.

On the 23d of May, 1855, comes the first application of a method which Professor Cooke afterward used often. The Corporation voted, "That $500 be appropriated to supply deficiencies in the cabinet of minerals, to be expended under the direction of Professor Cooke, provided that the additional sum of $500 be raised by private subscription for the same purpose." Nearly a year later Professor Cooke informs the Corporation that $1470 (subsequently increased to $1720) have been contributed by persons whose names are subjoined for the increase of the mineral cabinet, and he thereupon proposes that he have leave of absence for the summer term of 1857 to make purchases in Europe. In every summer vacation, and in some of the long winter vacations of that period, Professor Cooke travelled in search of minerals; and for a period of six years I frequently accompanied him. I was the first student whom he admitted to the little laboratory in the basement of University Hall, and Professor Frank H. Storer and I were his first assistants, both at the Cambridge laboratory and at the laboratory in the Medical School. I therefore have a vivid recollection of the humbleness of the beginnings of both the Chemical and the Mineralogical departments; of the elementary quality of the instruction given; and of the great disadvantages under which all the instruction was given, without any possibility of offering laboratory practice to the students, except as a favor which could be granted only to very few; but I also have a clear vision of the indomitable industry, perseverance, and mental activity of the young Professor. He threw himself body and soul into his work, and wanted neither recreation nor leisure, neither ease nor pleasure, but only work which would tell for the advancement of his department and the satisfaction of his worthy ambitions.

Early in 1856, he began to revolve plans for building a Chemical Laboratory at Cambridge; but a suggestion made to him by Mr. John Eliot Thayer turned his attention to the Boylston Fund (then amounting to nearly $23,000), which was held by the Corporation for the purpose of ultimately building an Anatomical Museum and Chemical Laboratory. This fund was to accumulate until it reached the sum of $35,000; but Mr. Thayer suggested that the fund be filled up by private subscription and the building contemplated by Mr. Boylston be at once erected. Accordingly, on the 30th of August, 1856, we find this entry in the records of the President and Fellows: "A letter from Professor Cooke having been read, the President, Treasurer, and Dr. Hayward were appointed a Committee to confer with Professors Wyman and Cooke on the subject of an Anatomical Museum and Chemical Laboratory." This project being made known abroad, a storm arose in the Medical Faculty, who feared the competition of the proposed Cambridge establishment. On the 15th of September following "a memorial from the Medical Faculty on the subject of certain proposed subscriptions was read and referred to the same Committee to which the letter of Professor Cooke was referred at the last meeting of this Board."

At a meeting of the President and Fellows on September 27th, "on application of Mr. Cooke, Erving Professor of Chemistry and Mineralogy, *voted*, that the Erving Professor be released from the duty of delivering lectures at the Medical College in Boston." Thereupon Professor Cooke caused all the excellent fixtures and furniture which he had provided in the building on North Grove Street to be torn out, and removed with all his apparatus to Cambridge. This vigorous procedure occurred shortly before the opening of the medical course of lectures, and threatened grave inconvenience to the Medical Faculty. At the same time, Professor Morrill Wyman resigned as a member of the Medical Faculty, because he was charged with disloyalty to the Medical Faculty in promoting the building of Boylston Hall. Altogether, the conflict waxed so warm, that Professor Cooke proposed an adjustment, which was carried into effect. By his advice I gave the first half of the course of chemical lectures at the Medical School, and Professor Cooke lent me, as his friend, all the apparatus and supplies necessary for the purpose. This sudden and unexpected disturbance led to two good results. It freed Professor Cooke from distracting and uncongenial labors at the Medical College; and it caused the appointment of a separate Professor of Chemistry for the Medical School, the first incumbent of that professorship being the excellent Dr. John Bacon, who began his labors in January, 1857. Thereafter, Professor Cooke was entirely free to devote himself to the interests of his departments at Cambridge.

In 1856 — the year now under consideration — Professor Cooke obtained from the College Faculty a really extraordinary concession for the ensuing academic year. He succeeded in introducing into the Junior year a required course on Molecular Physics, the text-book being the first volume of Graham's Elements of Chemistry. When one remembers that the traditional subjects filled well the prescribed curriculum, it is a marvel that a wholly new subject should have been inserted into the Junior year. Two years later the text-book for Molecular Physics became Cooke's Chemical Physics, — a work which showed the natural leaning of his mind to Physics rather than to Chemistry, and which also showed what importance he attached to exactness and thorough drill in undergraduate work. The book was intended to be used with numerous problems of an arithmetical or algebraic sort. The same year which saw the introduction of the Chemical Physics, namely, 1858–59, saw also an additional chemical elective for Juniors, — in the first term, Crystallography, and in the second term Analytical Chemistry and Dana's Mineralogy, — but in the meantime Boylston Hall had been built.

I must turn back for a moment to the year 1856. On the 25th of October, 1856, the Corporation voted, "That the President, Dr. Hayward, and Mr. Lowell, be a Committee to consider and report upon a plan and location for a building for the Anatomical Museum and Chemical Laboratory." and three months later it was voted "That the Committee on the new Anatomical Museum and Laboratory be authorized to make contracts for the erection of the same whenever the subscriptions for the increase of the Boylston Fund shall amount to $17,000." At the same meeting, "it appearing to this Board that in the new distribution of studies for the present year the proportion assigned to the Erving Professor of Chemistry and Mineralogy has been largely increased, so that the work now required of him equals the average of what is required of the other Professors, therefore, *Voted*, That the salary of the Erving Professor of Chemistry and Mineralogy be raised to $2,200, until further order of this Board." This vote, passed only seven years after the election of Mr. Cooke as Erving Professor, established him on terms of perfect equality with the Professors of the traditional subjects in Harvard College; and he was now only thirty years of age.

By the 31st of January, 1857, the necessary supplement to the Boylston Fund had been raised and the contract made for the erection of the building. On the 20th of May following, Professor Cooke reported to the Corporation on the inception and completion of this undertaking. The sum raised was $14,000. Thereupon it was voted, "That the Corporation avail themselves of this opportunity to express their sense of the efficiency and public spirit of Professor Cooke in obtaining the above mentioned subscriptions, and of his devotion to science and to his own department of instruction in the University, as manifested in his willingness to commence this movement, and in the unwearied efforts by which he has brought it to a successful issue." Long before the building was finished, — namely, on the 29th of August, 1857, "Mr. Lowell laid before the meeting a communication from Professor Cooke in regard to the necessary furniture for the new Anatomical Museum and Chemical Laboratory," whereupon it was voted "That the Building Committee be authorized to contract for the necessary furniture not exceeding the sum of $2,000." On the 1st of January following, the "Building Committee was authorized to pay a further sum, not exceeding $2,108, for altering, finishing, and fitting up the new Museum and Laboratory."

All this time Professor Cooke had had no visible assistance in the conduct of his department. He had himself paid for the services of Francis P. Clary, for many years his only assistant at his lectures, and he had received some volunteered assistance from students. In February, 1858, Charles W. Eliot, Tutor in Mathematics, was elected Assistant Professor in Mathematics and Chemistry, "to give such assistant instruction in the Department of Chemistry as may be agreed upon in the distribution of studies by the Faculty." The duties of this officer continued, however, to be chiefly mathematical, and it was not till January 26, 1861, that the Corporation voted, "That the duties of Mr. Charles W. Eliot be limited to the Chemical Department, and that he be designated accordingly."

On the 26th of June, 1858, a committee of the Corporation having reported that Professor Cooke had given furnaces, counters, and cases which originally belonged to him, and that part of the apparatus still belonged to him, it was voted, "That the President be requested to write a suitable letter of acknowledgment to Professor Cooke for his liberal contributions towards the erection and furnishing of Boylston Hall, and for his zeal and unremitting attention in overseeing the progress and successful accomplishment of the whole work." There are at this moment in Boylston Hall wooden counters and hoods with cast-iron sashes which Professor Cooke caused to be made forty-three years ago for the Laboratory which he first fitted up in the Medical College on North Grove Street. Boylston Hall was originally two stories high, and the western end was devoted to the Anatomical

Department, in charge of Professor Jeffries Wyman. About two thirds of the building, however, were devoted to the Chemical Department.

In 1858–59 the first laboratory instruction in Chemistry open to Harvard undergraduates, was given in Boylston Hall, and in that first class I find the following names, now well known in this community: —

James A. Rumrill,
William Everett,
William R. Huntington,
S. W. Langmaid,
John Homans, Jr.,
Henry P. Walcott, and
Louis Cabot.

The number of students in this first class was twenty-three, part of them graduates.

On the completion of Boylston Hall, the Mineral Cabinet was moved into it, so that all Professor Cooke's interests were concentrated in that building. The completion of Boylston Hall made it possible for Professor Cooke to teach mainly by the laboratory method; but recitations and problem work, not accompanied by laboratory practice, lingered, nevertheless, for seventeen years; although only in required courses. There was a required course in the Junior year down to 1867–68, and in the Sophomore year down to 1872–73. The required work was then moved into the second term of the Freshman year, whence it disappeared in 1875–76, a brilliantly illustrated course of lectures, always given by Professor Cooke, being thereafter the sole remnant of required work in Chemistry. The expansion of the elective work after the completion of Boylston Hall went on as follows: In 1868–69 a Senior elective appears, which was devoted in the first term to Crystallography and the Physics of Crystals, and in the second term to Mineralogy and the Determination of Minerals. In the year 1871–72 there are electives in Chemistry for the Sophomore, Junior, and Senior years, and Organic Chemistry appears in the Senior electives. In 1873–74 the electives are: —

1. Descriptive Chemistry.
2. Qualitative Analysis.
3. Mineralogy.
4. Quantitative Analysis.
5. Organic Chemistry.

In 1876–77, two new electives were added, — namely, an advanced course in Inorganic Chemistry, and a course in Crystallography and the Physics of Crystals, the second of these subjects having appeared for the first time as a half course in 1868–69. In 1886–87 the advanced course in Inorganic Chemistry was more completely defined as including Molecular Weights and Volumes, Thermo-Chemistry, and Specific Refractive Power. This course, thus introduced by Professor Cooke, has to-day a growing importance. In 1892–93, at the age of sixty-five, Professor Cooke undertook a new elective course in Chemical Philosophy and the History of Chemistry. This was the last addition he made to the series of elective courses he had successively introduced, the greater part of which he had delivered over into the hands of younger men. We cannot too much admire the intellectual vitality which enabled him to keep in the van of the onward movement in an extensive department which he had himself filled with younger teachers full of zeal and ambition.

The picture of Professor Cooke's influence at the head of the Chemical Department down to 1880, would be incomplete without an enumeration of the names of the young men who served as his laboratory assistants during the first thirty years that he held the professorship. Three of these gentlemen died young; but the following survive: —

Professor Frank H. Storer,
President Charles W. Eliot,
Professor William H. Pettee, of the University of Michigan,
Professor Charles L. Jackson,
Professor Henry B. Hill,
Professor Charles E. Munroe, of Washington,
Professor William Elder, of Waterville,
Professor Frank A. Gooch, of Yale University,
Professor M. E. Wadsworth, Head of the Michigan Mining School,
Professor Charles F. Mabery, Professor in the Case School of Applied Science of Cleveland;

and four gentlemen who have all been devoted to technical Chemistry, — namely, Messrs. Charles S. Homer, William D. Philbrick, John F. White, and Harry Blake Hodges. All these gentlemen were emphatically Professor Cooke's assistants. A large number of younger men have been trained as assistants in Boylston Hall during the last fourteen years; but many of them were brought into little immediate contact with Professor Cooke, because they served in laboratories which were chiefly directed by other Professors. Of late years he used to complain that there were assistants in Boylston Hall whose names he did not know, — an inevitable but unwelcome result of the growth of the establishment.

The growth of the College and the increased teaching of Chemistry by the laboratory method, made it necessary in 1871 to enlarge Boylston Hall. This was done by adding a roof story, at a cost of $13,500, of which sum Professor Cooke contributed $1,000 and his father $500. Professor Cooke also devised all the improvements himself, and zealously superintended their execution. For the uses of the Chemical Department, two thirds of the roof story were available; the trustees of the Peabody Museum hired the remaining third. This enlargement of Bolyston Hall made it possible to carry all the chemical teaching at Cambridge to that building, and, therefore, to close the Chemical Laboratory in the Lawrence Scientific School. This change was in part an economical measure, but was due, also, to the desire of the Corporation to use Count Rumford's gift for teaching the subjects of light and heat, and to make the Rumford Professorship again a College professorship. The consolidation was naturally a great satisfaction to Professor Cooke, and it was certainly an important step in the development, not only of the Chemical Department, but of the Department of Physics as well.

After the lamented death of Professor Jeffries Wyman in 1874, Professor Cooke began the process of acquiring for Chemistry the whole of Boylston Hall. The rooms on the lower story of Boylston Hall, which had formerly been used by Professor Wyman, were fitted up for a laboratory of Organic Chemistry. In the summer of 1877 the Peabody Collection was moved from Boylston Hall to the new building erected by the trustees; and thereupon the two large and handsome rooms on the western side of Boylston Hall were appropriated to the Mineral Cabinet, which had long outgrown its narrow quarters. The rearrangement of this collection made manifest the results of Professor Cooke's well directed and unremitting exertions for twenty-six years. The collection had become not only an effective instrument of instruction, but a beautiful and impressive representation of the mineral kingdom, unusually complete, and of large money value. From this date Professor Cooke had possession of the whole of Boylston Hall, except that a lecture room on the western end was still used for miscellaneous purposes. In 1887 this lecture room was converted into a laboratory for elementary experimental Chemistry, — again both planning and executing being Professor Cooke's. His occupation of the hall thus became complete, twenty-nine years from the date of its erection.

One year later, Professor Cooke entered on his last undertaking for the enlargement of his domain. He began to make plans and solicit subscriptions for a section of the University Museum on Oxford Street to be devoted to Mineralogy. His primary object was to obtain more space for the exhibition of minerals, and a new laboratory of Mineralogy; but a secondary object was to remove this valuable collection from a building which was not fireproof, and which was subject to the risks of chemical experimentation. His efforts were soon crowned with success; and in 1889–90 a section of the Museum devoted to Mineralogy, with a floor area of 13,200 feet, was finished at a cost of $35,000. This area provided not only an exhibition room, but a lecture room, laboratory, and store-rooms. The Mineral Cabinet having been removed from Boylston Hall, it became possible to provide in that building a large laboratory for Organic Chemistry, and a new lecture room seating five hundred students. These changes were made at the cost of the Corporation in 1891, Professor Cooke actively superintending them in all their details.

When a man has started early in enthusiastic pursuit of a worthy object, and has vigorously pursued it through all his active life, it is a sincere satisfaction to all who have observed him, and particularly to all who have been at any time his comrades or followers in the pursuit, to see him, before death comes, reach his goal. Professor Cooke attained and gave this happiness. He himself saw his beloved science taught in the only way he thought wise and effectual, and raised in academic standing to an equal level with the oldest and most valued subjects used in education. He saw large laboratories and lecture rooms, which he had himself planned and built, filled with eager students. And finally he saw the mineral collection, which had been his care and delight for forty-four years, safely and handsomely established in the principal University Museum. Few men see so many of their objects attained, so many of their hopes fulfilled. He had other sources of profound satisfaction, some of which have been already pointed out to-night; it was my part to describe his remarkable and enduring administrative achievements as Erving Professor of Chemistry and Mineralogy in Harvard College.

A LIST OF THE MORE IMPORTANT PUBLICATIONS OF JOSIAH PARSONS COOKE.

Books.

1857. Chemical Problems and Reactions.

1860. Elements of Chemical Physics. New editions in 1866 and 1877.

1864. Religion and Chemistry or Proofs of God's Plan in the Atmosphere and its Elements. New edition in 1880.

1868. Principles of Chemical Philosophy. New editions in 1870, 1875, and revised edition in 1881.

1874. The New Chemistry. New editions in 1876, 1877, 1884 and 1888. Also translations in many languages.

1881. Scientific Culture and Other Essays.

1888. The Credentials of Science the Warrant of Faith. New edition 1893.

1891. Laboratory Practice. A Series of Experiments on the Fundamental Principles of Chemistry.

Papers on his Original Investigations.[1]

1852. Description of a Crystal of Rhombic Arsenic. These Proceedings, III. 86.

1852. Octahedral Crystals of Arsenic. These Proceedings, III. 204.

1854. The Relation between the Atomic Weights. Mem. Am. Acad., New Series, V. Am. J. Sci., [2.], XVII. 387.

1854. On two new Crystalline Compounds of Zinc and Antimony. Am. J. Sci., [2.], XVIII. 229.

1854. On a new Filtering Apparatus. Am. J. Sci., [2.], XVIII. 127.

1855. On the Law of Definite Proportions in the Compounds of Zinc and Antimony. Am. J. Sci., [2.], XX. 222.

1860. Crystalline Form not necessarily an Indication of Definite Chemical Composition. Am. J. Sci., [2.], XXX. 194. Phil. Mag., XIX. 405.

1861. On the Dimorphism of Arsenic, Antimony, and Zinc. Am. J. Sci., [2.], XXXI. 191.

1862. On the Spectroscope. Am. J. Sci., [2.], XXXIV. 299.

1863. On the Cleavage of Galena. Am. J. Sci., [2.], XXXV. 126.

1863. An Improved Spectroscope. Am. J. Sci., [2.], XXXVI. 266.

1863. Crystallographic Examination of Childrenite. Am. J. Sci., [2.], XXXVI. 257.

1864. Crystallographic Examination of the Acid Tartrates of Caesia and Rubidia. Am. J. Sci., [2.], XXXVII. 70.

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[1] Prepared by T. W. Richards.

1865. On a Spectroscope with many Prisms. Am. J. Sci., [2.], XL. 305.

1865. On the Projection of the Spectra of the Metals. Am. J. Sci., [2.], XL. 243.

1866. On the Aqueous Lines of the Solar Spectrum. Am. J. Sci., [2.], XLI. 17.

1866. Separation of Iron and Alumina. Am. J. Sci., [2.], XLII. 78.

1866. Analysis of Danalite of Rockport. Am. J. Sci., [2.], XLII. 73.

1867. On Cryophyllite. Am. J. Sci., [2.], XLIII. 217.

1867. On Certain Lecture Experiments. Am. J. Sci., [2.], XLIV. 189.

1867. Crystallographic Examination of some American Chlorites. Am. J. Sci., [2.], XLIV. 201.

1867. A Method of Determining the Protoxyd of Iron in Silicates not Soluble in the Ordinary Mineral Acids. Am. J. Sci., [2.], XLIV., 347.

1869. Atomic Ratio. Am. J. Sci., [2.], XLVII., 386.

1874. The Vermiculites. These Proceedings, IX. 35.

1875. Melanosiderite. These Proceedings, X. 451.

1875. On two new Varieties of Vermiculites. With F. A. Gooch. These Proceedings, X. 453.

1876. On a new Mode of Manipulating Hydric Sulphide. These Proceedings, XII. 113.

1876. On the Process of Reverse Filtering. These Proceedings, XII. 124.

1877. Revision of the Atomic Weights of Antimony. These Proceedings, XIII. 1.

1877. Re-examination of Some of the Haloid Compounds of Antimony. These Proceedings, XIII. 72.

1879. The Atomic Weight of Antimony. These Proceedings, XV. 251.

1880. On Argento-antimonious Tartrate. These Proceedings, XIX. 393.

1880. On the Oxidation of Hydrochloric Acid Solutions of Antimony in the Atmosphere. Am. J. Sci., [3.], XIX. 464.

1881. On the Solubility of Chloride of Silver in Water. Am. J. Sci., [3.], XXI. 220.

1881. Additional Experiments on the Atomic Weight of Antimony. These Proceedings, XVII. 1.

1881. The Boiling Point of Iodide of Antimony and a new Form of Air Thermometer. These Proceedings, XVII. 22.

1883. A Simple Method for Correcting the Weight of a Body for the Buoyancy of the Atmosphere when the Volume is Unknown. Am. J. Sci., [3.], XXVI. 38.

1883. Possible Variability of the Law of Definite Proportions. Am. J. Sci., [3.], XXVI. 310.

1887. The Relative Values of the Atomic Weights of Oxygen and Hydrogen. With T. W. Richards. These Proceedings, XXIII. 149.
1888. Additional Note on the Relative Values of the Atomic Weights of Oxygen and Hydrogen. With T. W. Richards. These Proceedings, XXIII. 182.
1889. On a New Method of Determining Gas-densities. These Proceedings, XXIV. 202.

Papers on Other Subjects.

1862. Review of Trollope's North America. No. Am. Rev., XCV. 416.
1865. On the Heat of Friction. These Proceedings, VI.
1871. Memoir of Thomas Graham. Am. J. Sci.
1871. Absolute System of Electrical Measurements. Collected Papers from Journal of Franklin Institute.
1874. The Nobility of Knowledge. An Address delivered before the Free Institute of Worcester. Pop. Sci. Month., V. 610.
1875. Scientific Culture. Pop. Sci. Month., VII. 511.
1875. "Gas." Johnson's Cyclopædia.
1875. "Molecules." American Cyclopædia.
1877. Chemical and Physical Researches by Thomas Graham. Am. J. Sci., [2.], XIV. 152.
1878. The Radiometer: a Fresh Evidence of a Molecular Universe. Pop. Sci. Month., XIII. 1. Also Am. J. Sci., [3.], XIV. 231.
1878. Chemical Philosophy. Am. J. Sci., [3.], XV. 211.
1880. In Memoriam Josiah Parsons Cooke.
1880. Notice of Berthelot's Thermo-Chemistry. Am. J. Sci., [3.], XIX. 261.
1881. Memoir of William Hallowes Miller. These Proceedings, XVI. 461.
1881. Notice of the Investigation of Dr. J. W. Brühl on the Relations between Molecular Structure of Organic Compounds and their Refractive Power. Am. J. Sci., [3.], XXI. 70.
1881. Notice of Julius Thomsen's Thermo-chemical Investigation of the Molecular Structure of Hydrocarbon Compounds. Am. J. Sci., [3.], XXI. 88.
1883. The Greek Question. Pop. Sci. Month., XXIV. 1.
1883. Memoir of John Bacon. These Proceedings, XVIII. 419.
1883. Memoir of William Barton Rogers. Ibid., 428.
1884. Memoir of J. B. A. Dumas. These Proceedings, XIX. 545.
1884. Memoir of C. A. Wurtz. Ibid., 568.
1884. Further Remarks on the Greek Question. Pop. Sci. Month.
1885. Memoir of Benjamin Silliman. These Proceedings, XX. 523.
1886. Descriptive List of Experiments for Use in Chemistry B.

1886. The New Requisitions for Admission at Harvard College. Pop. Sci. Month., XXX. 195.
1889. The Chemical Elements. History of the Conception which this Term involves. Pop. Sci. Month., XXXIV. 733.
1889. Address at the Commencement Dinner.
1889. Concluding Address to the Freshman Class of Harvard College.
1890. Report of the Director of the Chemical Laboratory of Harvard College. Presented to the Visiting Committee of the Overseers.
1890. A Plea for Liberal Culture.
1892. The Value and Limitations of Laboratory Practice in a Scheme of Liberal Education.
1892. Memoir of Joseph Lovering. These Proceedings, XXVII. 372.

Also many Reviews and Reports, including Annual Reports as Director of the Chemical Laboratory during many years.

Eight hundred and seventy-first Meeting.

January 9, 1895. — STATED MEETING.

The PRESIDENT in the chair.

The election of two Vice-Presidents to fill the vacancies occasioned by the amendment of the Statutes adopted on the 10th of October, 1894, resulted in the choice of

BENJAMIN A. GOULD, Vice-President for Class I.
GEORGE L. GOODALE, Vice-President for Class II.

The following gentlemen were elected members of the Academy: —

Robert Tracy Jackson, of Boston, to be a Resident Fellow in Class II., Section 1 (Geology, Mineralogy, and Physics of the Globe).

John Eliot Wolff, of Cambridge, to be a Resident Fellow in Class II., Section 1.

Samuel Fessenden Clarke, of Williamstown, to be a Resident Fellow in Class II., Section 3 (Zoölogy and Physiology).

William Thomas Councilman, of Boston, to be a Resident Fellow in Class II., Section 3.

Charles Benedict Davenport, of Cambridge, to be a Resident Fellow in Class II., Section 3.

John Sterling Kingsley, of Somerville, to be a Resident Fellow in Class II., Section 3.

George Howard Parker, of Cambridge, to be a Resident Fellow in Class II., Section 3.

William McMichael Woodworth, of Cambridge, to be a Resident Fellow in Class II., Section 3.

Charles L. Jackson proposed certain changes in the Statutes. This subject was referred to a committee, consisting of C. L. Jackson, A. Lowell, and F. H. Storer.

Henry P. Bowditch, Chairman of the Committee on the Library, read a statement in reference to the expenditures on account of the library, during the last five years. After some discussion, the matter was referred to a committee, consisting of the Librarian, the Treasurer, and the Chairman of the Rumford Committee, with instructions to consider the advisability of appropriating a portion of the income of the Rumford Fund toward defraying the expenses of the library.

On the motion of Charles S. Minot, it was

Voted, To refer the matter of expenditures both for Publications and for the Library to a committee, consisting of the Committee of Publication and the Committee on the Library, the chairman of this committee to be the Chairman of the Committee of Publication.

Edward L. Mark alluded to the "List of serial Publications taken in the Principal Libraries of Boston and Cambridge," published in 1878, and spoke of the need of a new and revised edition of this list. After some discussion, it was

Voted, To call the attention of the Trustees of the Boston Public Library to this matter.

Franklin B. Stephenson read a paper entitled, "Congenital Spots on Annamites, a Means of Racial Identification."

The following papers were read by title: —

Studies on Morphogenesis. III. On the Acclimatization of Organisms to High Temperatures. By Charles B. Davenport and W. E. Castle.

On the Occlusion of Baric Chloride by Baric Sulphate. By T. W. Richards and H. G. Parker.

Eight hundred and seventy-second Meeting.

February 13, 1895.

Vice-President B. A. Gould in the chair.

The chair announced the death of Arthur Cayley and of Sir John R. Seeley, Foreign Honorary Members.

The Corresponding Secretary read the following letters: from S. F. Clarke, of Williamstown, acknowledging his election as Resident Fellow; and from the National Society of Horticulture of Paris, announcing the death of its Secretary, Pierre Etienne Simon Duchartre. He also read an invitation circular from the organizing committee of the Sixth International Geographical Congress.

Edward Atkinson described the application of heat to the process of cooking according to the principle of Count Rumford, illustrated by demonstrations.

He also exhibited a specimen of calcium carbide (CaC_2). This substance, being dropped into water, readily decomposes, liberating pure acetylene with the formation of calcium hydrate, the reaction being $CaC_2 + 2\,H_2O = C_2H_2 + CaO_2H_2$. The acetylene was lighted with a match, and burnt on the water.

Eight hundred and seventy-third Meeting.

March 13, 1895. — Stated Meeting.

Vice-President B. A. Gould in the chair.

The chair announced the death of Sir Henry C. Rawlinson and of the Marquis de Saporta, Foreign Honorary Members.

The chair appointed a Nominating Committee, consisting of William R. Livermore, Henry P. Walcott, and Thomas W. Higginson.

The report of the Committee on amending the Statutes was read, and the committee discharged.

In accordance with the recommendation of the Committee, it was

Voted, To amend the second section of Chapter IX. of the Statutes by omitting the words, "and any Resident Fellow who shall remove his domicil from the Commonwealth shall be deemed to have abandoned his Fellowship."

A recommendation to rearrange the sections in Class I. was laid on the table until the next meeting.

The Committee on Appropriations for Publications and for the Library made a report, and, in accordance with a recommendation contained therein, it was

Voted, That the committee issue a circular to the Fellows of the Academy, soliciting subscriptions to meet the expenses of publication.

Voted, To discontinue the purchase of books for the library excepting such as shall be approved by a vote of the Committee on the Library.

On the motion of the Corresponding Secretary, it was

Voted, To meet on adjournment on the second Wednesday in April.

Charles L. Jackson tendered his resignation from the Committee on Appropriations for Publications and for the Library, which was accepted, and the chair appointed Henry W. Haynes member and chairman of the committee.

Henry W. Haynes read a report of the committee appointed to consider the advisability of appropriating a portion of the income of the Rumford Fund toward defraying the expenses of the Library.

The following gentlemen were elected members of the Academy: —

Sir Henry Bessemer, of London, to be a Foreign Honorary Member in Class I., Section 4 (Technology and Engineering), in place of the late Ferdinand M. de Lesseps.

Sven Lovén, of Stockholm, to be a Foreign Honorary Member in Class II., Section 3 (Zoölogy and Physiology), in place of the late Pierre J. Van Beneden.

Sir Frederick Pollock, Bart., of Oxford, to be a Foreign Honorary Member in Class III., Section 1 (Philosophy and Jurisprudence), in place of the late Sir James F. Stephen.

W. R. Livermore gave an informal talk on the political changes of Europe, from 350 to 1100 A. D., illustrated by a series of seventy-five colored maps, showing the boundaries of each tribe and nation for every ten years.

The following announcement by Henry Taber was read by William E. Story: —

> In Volume XVI. p. 130, of the *American Journal of Mathematics* I have shown that certain conditions are satisfied by every orthogonal substitution which is given by the positive square of Cayley's symbolic expression for orthogonal substitutions, in other words, by every orthogonal substitution which is the second power of an orthogonal substitution. I have since found that these conditions are sufficient that a given orthogonal substitution shall be the second power of an orthogonal substitution.

The following papers were read by title: —

On the Action of Ammonia upon Cupriammonium Acetobromide. By Theodore W. Richards and Robert J. Forsyth.

Velocity of Electric Waves. A direct Determination of this Value and a Discussion of its Relation to the Velocity of Light. By John Trowbridge.

Eight hundred and seventy-fourth Meeting.

April 10, 1895. — ADJOURNED STATED MEETING.

The PRESIDENT in the chair.

In the absence of the Recording Secretary, William R. Livermore was appointed Secretary *pro tempore.*

The chair announced the death of James Edward Oliver, of Ithaca, Associate Fellow.

The Corresponding Secretary read a circular from Emil Diebitsch, soliciting on behalf of Mrs. Josephine Diebitsch Peary subscriptions in aid of a proposed expedition for the relief of Mr. Peary and the promotion of Arctic scientific research.

On the motion of B. A. Gould, it was

Voted, That the Corresponding Secretary be directed to express to Mrs. Peary the regrets of the Academy that the state of its funds do not permit it to contribute toward the expenses of this expedition.

On the motion of the Corresponding Secretary it was

Voted, To take from the table the report of the Committee on rearranging the sections in Class I.

Voted, To amend Chapter I., Section 1, of the Statutes by changing "Section I. Mathematics; — Section 2. Practical Astronomy and Geodesy; — Section 3. Physics and Chemistry," to "Section 1. Mathematics and Astronomy; — Section 2. Physics; — Section 3. Chemistry."

The Corresponding Secretary proposed that Chapter 9, Section 2, line 8, of the Statutes be amended by changing the word "eight" to "seven." This proposition was referred to a committee, consisting of C. S. Minot, S. C. Chandler, and A. M. Davis.

A report on the subject of appropriations for the ensuing year was read by H. W. Haynes, Chairman of the Joint Committee consisting of the Standing Committees of Publication and on the Library. After discussion, it was

Voted, That the Committee of Publication, the Committee on the Library, and the Treasurer be instructed to report to the Committee of Finance estimates of expenses for the coming year.

Voted, That the money recently raised by subscription be appropriated to printing the current volume of *Proceedings*.

Alexander Agassiz and William M. Woodworth read a paper entitled, "Some Variations in the Genus Eucope."

The following papers were presented by title: —

On Bivalent Carbon. Third Paper: The Chemistry of Cyanogen and Isocyanogen. By J. U. Nef.

A Revision of the Atomic Weight of Zinc. By T. W. Richards and E. F. Rogers.

On the Automorphic Linear Transformation of a Bilinear Form. By Henry Taber.

On the Types of Linear Substitution which transform automorphically a Bilinear Form with Cogredient Variables. By Henry Taber.

AMERICAN ACADEMY OF ARTS AND SCIENCES.

Report of the Council. — Presented May 8, 1895.

BIOGRAPHICAL NOTICES.

Josiah Parsons Cooke	See Page 513.
Oliver Wendell Holmes	By Percival Lowell.
Edward Jackson Lowell	Henry W. Haynes.
Robert Charles Winthrop	William Everett.
William Holmes Chambers Bartlett	William R. Livermore.
Ezekiel Gilman Robinson	Thomas D. Anderson.
William Dwight Whitney	Thomas R. Lounsbury.
Charles Edouard Brown-Séquard	James J. Putnam.
Hermann Ludwig Ferdinand von Helmholtz	Henry W. Williams.
Marquis de Saporta	Sir John W. Dawson.

Notices of Dana, McCosh, Newton, Oliver, Cayley, De Lesseps, Marignac, Rawlinson, and Seeley are deferred to the next volume; that of Bartlett, deferred from last year, is given below.

REPORT OF THE COUNCIL.

SINCE the Annual Meeting of the 9th of May, 1894, the Academy has lost by death sixteen members; — four Fellows, Josiah Parsons Cooke, Oliver Wendell Holmes, Edward Jackson Lowell, and Robert Charles Winthrop; six Associate Fellows, James Dwight Dana, James McCosh, John Newton, James Edward Oliver, Ezekiel Gilman Robinson, and William Dwight Whitney; and six Foreign Honorary Members, Arthur Cayley, Hermann Ludwig Ferdinand von Helmholtz, Ferdinand Marie de Lesseps, Sir Henry Creswicke Rawlinson, Bart., Louis Charles Joseph Gaston, Marquis de Saporta, and Sir John Robert Seeley.

RESIDENT FELLOWS.

OLIVER WENDELL HOLMES.

OLIVER WENDELL HOLMES was born on August 29, 1809, in the first decade of the nineteenth century, and died on November 7, 1894, in its last. The century's contemporary, he was essentially exponent of the spirit of his time. But he was more. He was pre-eminently the spokesman of the place in which he lived. Though born in Cambridge, Massachusetts, his life was spent in Boston, and it was there he died. Bostonian by birth, if not by birthplace, he was himself that typical individual of whom, more than half in earnest, he recorded the innate conviction that "Boston State-House" was "the hub of the solar system."

It is usually considered necessary to preface an account of a man with an account at some length of his ancestors, in a spirit truly Chinese. For though every man be a part of all that have met to his eventual construction, it is precisely because he differs from any of his progenitors that he is noteworthy. It is the combination he embodies, to say nothing of the advance, that singles him out as a man of mark.

Special stress, therefore, need not be laid on the fact that Holmes was the lineal descendant of "The Tenth Muse, lately sprung up in America," as Anne Bradstreet called her book of poems, since that lady was the poet's great-great-great-great-grandmother. Nor must we chronicle all the Dutchmen who appear with such safe wisdom in the middle of his name. Yet is it pleasing to note that his father was the Rev. Abiel Holmes, "a sunny old man," from whom, if from any one, he inherited his own sunny disposition.

It is sufficient here to begin with the dame to whom Holmes early went to school, whose Prentiss hand, armed with an enormous birch, seems rarely or never to have been tried on the youngsters she undertook to form, — a pleasing exception to the spirit of the times. From this almost fossiliferous educational period it gives one something of a start to find the subject of it five years later in all modernity at Phillips Academy, Andover. It was there that Holmes began to write, poetry of course and heroics, a translation of the first book of the Æneid. In 1825 he entered Harvard, and started on that career of verse for which we remember him, — verse called occasional; in Holmes's case with certainly double-edged humor, as the occasions were substantially continuous from the start.

He began very early to write well; some of his best pieces being written for the Collegian, the college paper of the day, — among others "The Height of the Ridiculous" and "The Spectre Pig." In due course he became a member of the Φ B K. On graduating he coquetted with law, but soon gave it up for medicine, to which he remained faithful for the rest of his life, *non sine gloria*, illumined by *facetiæ*, for to him the funny-bone by definition bordered on the humerus. Upon his valuable contributions to the profession, and upon his all-pervasive scientific sense on the subject, it is not necessary here to dwell. For thirty-five years he held the chair of Anatomy and Physiology in the Harvard Medical School, delighting successive generations of students, and when at last he resigned, in 1882, the ovation he received showed how dearly he was loved.

One episode in his medical career, however, is important, from a literary standpoint. In 1833 he went abroad to study medicine in Paris. The importance of this lies not in the fact, but in its effect upon Holmes, and the importance of the effect not upon its positive, but upon its negative side. He got what was to be got without bartering for it a tittle of his individuality.

> "Cœlum non animum mutant qui trans mare currunt,"

was never truer than of him. Indeed, had Horace not written this line, Holmes might have been counted on to do so. Both men were so whole with their native surroundings as to preclude their becoming to any transforming degree part of any other they might meet. This was even more the case with Holmes than with Horace. For Horace took much from the Greek, while Holmes never followed the French. But to both the great world without was corrective, not creative of that corner of it each was respectively born to within. In both there was that same tiresomeless carrier-pigeon flight across the waters from wherever the body might be, flight ever mindful of home and never resting till it reached there, which above all other traits is the characteristic of the poet of his own time and place. At home both were pre-eminently at home, which made them both delightful diners out. And if Horace was somewhat more mindful of Chloe than of the Schoolmistress, to the times is due the change. Holmes could find the woman amid perhaps the most austere society the world has ever known, unless it be that of the same society's ancestors, in which to be human was itself perilously near sin. So people wore masks, shocked by the sin in sincerity. Holmes and Horace might well have sat at the same table. And just as Quintus *par excellence*, Quintessence that he was of later Roman life, reveals to us that life as much more human than our early Latin text-books led us to suppose, so Holmes discovers charms in the Schoolmistress unsuspected of her pupils.

Having gone abroad once at the beginning of his life, Holmes did not go again till toward the close of it, a half-century later. The half-century that intervened constituted his life, and that was spent to all intents and purposes in Boston. His flights were chiefly limited, like Apollo's, to annual migrations from his winter home in his own temple in town to his summer sanctuary by the sea, and back again, — Beverly Farms being his local Delos. Yet though he thus practically never stirred from home, it was he who was always asked to welcome his country's guests, — welcome which none could more gracefully extend.

Of his honors the catalogue is long. He was elected into the American Academy on November 14, 1838, and became its Recording Secretary in 1845, an office he held till 1848. From 1880 to 1887 he was its Vice-President. In 1880 he was made an LL. D. by

Harvard, and in 1886 an LL. D. by Edinburgh, a Litt. D. by Cambridge, England, and a D. C. L. by Oxford. Not the least of the marks of the regard in which he was held by his fellows is the fact that when he died, as full of years as of honors, his death was felt as a national loss.

According to a remark credited to Longfellow, — though one finds it hard to conceive that he ever can have made it, — "Autobiography is what biography ought to be." True as this is of any man, it is well-nigh a truism of a man of letters. For, like the evening paper, the autobiographer chronicles little that is not already told. In the case of a man of action, even though that action take the intellectual form of prying into nature's laws, it is possible to catalogue the subject's deeds or discoveries. But with a writer who, instead of doing, said all that made his life important, a biographer has the doubtful choice between apologetically transcribing his original, or boldly taking him for a text to some disquisition of his own. If he have nothing to say, he embraces the former alternative; if something, the latter. Properly speaking, there is in the way of facts not much beyond the unavoidable birth and death, and usually unavoided marriage, together with a list of dated honors duly bestowed. The real life of the man was lived within, not without, and that the man has himself already revealed in the best of all ways, — unsuspectingly. Especially is this true of Holmes. His biography is his own books. There one shall find his life told better than any other will ever be able to tell it.

One point I shall mention and only one, for it seems to me peculiarly to distinguish the man. Holmes's genius was that of broad-minded localism. The term local may seem at first to carry with it the inference of the limited, but in truth it involves no more circumscription than individuality itself, the one applying to the man, the other to the community. An individual to be anybody must first of all be himself. In like manner, one who represents a place must, to start with, be permeated with the spirit of the place. In this sense he must be local, and in this sense Holmes was. It was the local that made the essence of the man, — the broad-mindedness that based it inseparably upon the universal, and made it not a part-truth, but a part of all truth. What is thus in the true sense local, though builded in one place, is builded for all time, taking on, from the fact that it once was, brevet of immortality. Thus did Holmes represent New England during the middle of the nineteenth century. He was himself New Englander to the core; so essentially so that he seemed not only to outsiders, but to New Englanders themselves, to stand for all that was most their own. If a man can be said to be a community, Holmes was New England.

Recognition began, unlike the proverbial prophet, with those nearest him. Chosen class-poet before graduation, he remained class-poet his whole life long, poet of the now historic Class of '29. Distinguished as the class was, Holmes's verses have carved for it a peculiar niche in the long gallery of commemorated class fame. These poems form a remarkable anthology. They extend over a period of sixty years, but the most striking point about them is the way in which each falls naturally into its place in the series as if designed to do so. There could be no greater witness to the fundamental fitness of each to its occasion. Reflected there we seem to see the class grow up, grow on, grow old. Pleasantry at the beginning slowly gives place to pathos toward the close. Yet, true mirror of life, neither is wholly absent; it is but a little more of the one, a little less of the other, as the procession of the years passes on. In these verses, too, we note with peculiar force that apotheosizing of the local which seems so easy and is so hard. Written for his fellows, their tellingness at the time loses none of its appositeness when retold in print to another generation of men. It is this carrying quality in his verse that marks, not aforethought, but something much deeper, the unconscious fulness of the thought itself. It was not meant to be universal; but it was universal because it was meant.

Passing on to his poems generally, we find at every turn proof of their New England stuff; and, as New England was and largely still is representative of America, proof of their national character. First, in their wit. The New Englander is emphatically witty: to him life itself is a sort of *double entente*. "Maybe to say one thing and mean another comes nat'ral to women": certainly to say a thing by not saying it comes natural to the New Englander. Both quick and sensitive, he shies from direct statement as being both dangerous and dull. His conversation is of the nature of an intellectual wrestling match, in which his chief object is to give no hold to his opponent. Furthermore, he lives in a new country, in which he is constantly encountering the unexpected, and in consequence the unexpected reflects itself in his speech. Now of this all-pervasive humor Holmes is the embodiment. Of all our poets he most is the exponent of the unexpected. Consult him *passim* for proof of it; then compare him with others, and the reader shall find that, to quote substantially unchanged his own words about another,

"Now we have lost him, our lament must be
We have five hundred — *not* as good as he."

That communities less witty should occasionally be shocked by his play of fancy is, reversely, to be expected. Possibly, the New Englander himself is a mistake, and all life as serious a thing as the statutes declare. But it tires one to think so.

Punning, unlike other crimes, is commonly denounced by such as are themselves incapable of committing it. Doubtless there are puns that are poorer than others, some of Shakespeare's being, by the accepted standard, among the worst, — but even a pun is not always hopelessly depraved. Still less so is humor which deals with the impression rather than with the expression of the thought. Yet, I suppose no humorist has lacked friendly critics to apologize to the public for his wit. I have just read some very kind excuses made for Holmes on this score, and am wondering why man is the only laughing animal if he must needs be so ashamed of his propensity. The philosopher perceives the profound unimportance of things, including his own opinions; it is the Governor's aide who takes himself seriously.

Pathos and pleasantry are twins. The mind that conceives the one feels the other. Even the funniest of Holmes's verse stands against a background of feeling. He was so human. His set productions of a pathetic character are singularly few, — as few as the actual occasions in life that to a healthy mind call them forth. But all his verse is touched by emotion hinted at, not expressed, as to any sensitive soul is life itself. Even his "Last Leaf" is not primarily pathetic but humorous, yet the stanza,

"The mossy marbles rest
On the lips that he has pressed
In their bloom,
And the names he loved to hear
Have been carved for many a year
On the tomb,"

brings a lump into the throat and a dimming of the eyes, no matter how often one repeat the lines. It is to miss the point to consider this poem, as I have seen done by a critic from across the sea, as a pathetic production, and then explain away the humor in it as irrelevant. The humor it is that has the right of way, but makes way insensibly for the feeling.

Another point in which Holmes stood representative of his unwritten constituents was his skill in apt simile. A shunning of the positive leads the New Englander unconsciously into parable. Rather than blurt out bluntly what he means, he prefers to constrain consent by a process of easy analogical admission. This may or may not take the form of the comic. In the average Yankee it usually does so, but his parabolic cast of thought is really something distinct from humor. Witness the landlord in Fitz Adam's story, who described his son as

> "A long slab-sided youngster with a gun,"

and whose recipe for cooking birds was

> "Jes' scare 'em with the coals, — that 's my idee."

Of course this deviation from directness easily passes into the hyperbolic, as when we are told that a thing is as difficult as hunting in the dark for a black hat *which is n't there.* Such hyperbolic intent is not to be confounded with the conversational curve of pursuit — but non attainment — of the unconsciously blundering bull.

But though Holmes's wit was based on the broad foundations of his country's wit, his was no rescript of it such as we are presented with in real or fictitious dialect tales. These too are national in an objective sense. Holmes was subjectively so. He was always himself, but that self was essentially the outcome of his surroundings. He was typical and typical of the best, — the national poet of the educated class of his countrymen, to a degree which I do not recall ever to have been matched.

New England air is conducive to a shrewd sort of philosophizing. There is much pithy wisdom, if there be naught else, to be gleaned from the hillsides of the boulder-strewn New England farm. All this was Holmes's inheritance; genius and culture did the rest. We are given it capitalized in the "Autocrat of the Breakfast Table," and on in delightful instalments, till we sit with him at last "Over the Teacups" in the sunset of his life. These books of practical philosophy are probably without a peer in the world as a combination of wisdom with wit. But their characteristic that most impresses one is, like the poems, their remarkably genuine ring. They are delightfully humorous, without a hint of burlesque. You feel as you read on that this is no travesty of life seen through an astigmatic eye, however keen-sighted, but the real thing mirrored in a singularly pellucid retina that reflects without distortion. These books are most fittingly commemorative of their author. Poet always, his volumes of verse are beautiful mosaics; his essays are his monoliths.

In this brief attempt at tribute to one we shall all miss so long as we live, I have tried simply to point out what seems to me the essence of his genius, the fact that it was not the genius of dissimilarity, but the more uncommon one of supreme comprehensiveness of his kind. And this word is touchstone to more, since in its other sense as well it was so fully what he was, — whose like, like as he was to others, we shall never look upon again, — our own Holmes, witty, genial, kind.

1895. PERCIVAL LOWELL.

EDWARD JACKSON LOWELL.

EDWARD JACKSON LOWELL was born in Boston on October 18, 1845. His father was Francis Cabot Lowell, one of a family noteworthy among the founders of the cotton-manufacturing industry of this country, and distinguished for acts of public beneficence. His mother was Mary, daughter of Samuel P. Gardner, of Boston. The youngest of five children, and having lost his mother before he was nine years old, he was placed, in accordance with her wish, at an excellent private school in Switzerland. The three years there spent, and the knowledge of the French and German languages there acquired, had doubtless a controlling influence upon the subsequent occupations of his lifetime. After completing his preparation at a private school in Boston, he entered Harvard College, and graduated with the Class of 1867. At college he gained some distinction as a writer of verse, both for the college paper and as occasional poet of society anniversaries, and upon graduation was selected to write the Class Ode. After spending some months in travel in Europe, he was married, on January 14, 1868, to Mary, daughter of Samuel G. Goodrich, whose writings, under the name of Peter Parley, were the delight of children of the last generation.

Mr. Lowell at first turned his attention to business, which he soon abandoned for the study of law, and was admitted to the bar in Boston in 1872. But having been so unfortunate as to lose his wife early in 1874, he thereupon determined to devote himrelf completely to the care and education of his three young children, a daughter and two sons, and to literary culture in general.

On June 19, 1877, he was married a second time, to Elizabeth, daughter of George Jones, of New York, one of the founders and principal directors of the New York Times, who survives him. Carrying out his educational plans, in 1879 he took his family to Europe, and passed two winters in Dresden and two in Paris, travelling extensively in the summer.

During his residence in Germany he became interested in the history of the German mercenaries employed by Great Britain in this country during our Revolutionary War, and in consequence he undertook extended researches among the archives of some of the smaller German states. The most important of these are now preserved at Marburg, in Hesse-Nassau, where are to be found many reports and journals received by the Landgrave Frederick II. of Hesse-Cassel from his officers during the entire course of the war. Others are to be found in the State library at Cassel, and in that of the Prince of Waldeck, at Arolsen, and a few in other localities. Of many of these documents, containing "original German accounts of every important engagement, and of almost every skirmish, of the Revolutionary War from the year 1776 to the end," he caused transcripts to be made, and was thus enabled to make use of sources of information that had never fallen under the eye of any American writer. The results of these researches were first given to the world in a series of letters to the New York Times, in the winter of 1880–81. After his return to this country, in 1884, they were published in a more extended shape in a volume entitled "The Hessians and the other German Auxiliaries of Great Britain in the Revolutionary War, with Maps and Plans," New York, 1884. This was a genuine contribution to the history of our country, and it attracted universal interest among our historical students. It was, indeed, a surprise to learn that a force of between fifteen and twenty thousand Germans served for seven years against us, and that more than twenty-nine thousand were brought to this country for that purpose, of whom more than twelve thousand never returned. As but a comparatively small portion of these were killed, we are thus able to account for a goodly contribution to the number of our German fellow citizens. The work was systematically conceived and thoroughly executed, and it was enlivened with anecdotes and adventures drawn from the experience of private individuals, in accordance with the intention of the author "to give an idea of what sort of people the auxiliaries were, and of what impression America and the Americans made upon them." It had a decided success, and as a speedy recognition of its merits the author was chosen a member of the Massachusetts Historical Society, in November, 1884.

Besides contributing articles to some of the leading magazines, Mr. Lowell's studies were now principally directed to the preparation for Dr. Winsor's "Narrative and Critical History of America" of a chapter upon "The Political Struggles and Relations of the United States with Europe, 1775–1782," which appeared in 1888. This bears evidence of extended reading in English and French historical sources, in addition to his German studies. It is principally devoted to narrating the attempts made by the United States during the earlier part of the Revolutionary War to obtain recognition and aid from foreign countries, and to raise the money for carrying on the struggle. Incidentally, the diplomatic situation in Europe, so far as it affected us, is portrayed, and the desperate financial straits to which we were reduced are well described. The result is a succinct and instructive survey of our early foreign relations. Besides embodying the results of his studies of the German auxiliaries, he became so deeply interested in the career of Lafayette that he formed the intention of writing his life. For that purpose, he began to collect materials, but abandoned the design upon learning that a similar work by another was on the eve of publication. He had intended to draw a contrast between the American and French Revolutions, but he changed his plan, and began the composition of what turned out to be his most important literary undertaking.

This was published in 1892 under the title of "The Eve of the French Revolution." It contains the ripe fruit of the studies and reflections of his life; from it we can learn the manly strength that underlay his singularly sweet and winning personality, and on it his reputation will chiefly rest. Whoever wishes to obtain a clear idea of the hidden causes that resulted in that fearful outburst of political passion cannot fail of satisfaction if he will carefully study this small but weighty volume. The author lays no claim to original research and pretends to formulate no novel views, but relies upon the results reached by the best historians and thinkers of France; and the reader will find many popular delusions in regard to the actual situation of that country immediately before the meeting of the States General completely dispelled. "The condition of the people," we are told, "both in Paris and in the provinces was far less bad than it has often been represented." They were not crushed by the oppression of a dissolute and tyrannical aristocracy, as many writers have asserted, nor was the Bastille crowded with captives, so that a political hurricane was needed to clear the moral atmosphere. But, on the other hand, we are made to see clearly what were the inherent vices of that *ancien régime*, which harassed and irritated every class in the community, and in the language of De Tocqueville produced "a condition of society which was detested by every one who knew it." In different chapters and with ample detail the author shows how the army had become discontented, because only nobles were eligible to high rank; how the magistracy had been for more than a generation engaged in a contest with the crown; how the men of letters without exception had become hostile to the government; how the taxation, though not so absolutely burdensome as has been assumed, was so manifestly unequal as to excite the bitterest indignation at the odious privilege of exemption enjoyed by the nobles and the ecclesiastics; and minor sources of dissatisfaction are brought to light in abundance. The author's summing up is that, " while France was great, prosperous, and growing, and a model to her neighbors, she was deeply discontented. . . . She had become conscious that her government did not correspond to her degree of civilization. . . . The financial situation was not the cause of the Revolution, but its occasion. All the machinery of the state needed to be inspected, repaired, or renewed. The people entered into the task with good will and the warmest interest. But they were entirely without experience. . . . In their ignorance of the working of popular assemblies, they supposed them to be inspired with wisdom and virtue beyond that of the individuals who compose them. . . . They accomplished for France much that was good, they prepared the way for much that was evil."

For many years Mr. Lowell was a very efficient member of the Board of Trustees of the Boston Athenæum, and by his refined appreciation and extended knowledge of art he was able to bring about a most marked improvement and increase in the art collections of that institution. In the winter of 1893 he again visited Europe, and passed quite a long time in Athens in the congenial companionship of the professors and students of the American School of Classical Studies, to which he had given his services for several years as treasurer. During this time he also procured additional treasures for the art collection of the Athenæum.

He was called home by illness in his family, and not long afterwards developed that mysterious sickness, arising from a tumor in the brain, which resulted in his sudden and regretted death at Cotuit, Mass., on May 11, 1894.

Mr. Lowell was elected a member of this Academy on March 9, 1887. He rendered the writer valuable assistance upon the Library Committee, and contributed to Volume XXVIII. of the Proceedings of the Academy, in May, 1893, a Memoir of Lord Tennyson, the last of his literary productions. Of these a chronological list is appended, so far as known to me.

1880–81. The Hessians. N. Y. Times.
1884. The Hessians; extended to a volume.

1887. Journal of Captain Pausch. — Introduction.
1887. German MS. Documents. Proc. Mass. Hist. Soc.
1887. Memoir of L. M. Sargent. Proc. Mass. Hist. Soc.
1887. Adventures of a Hessian Recruit. Proc. Mass. Hist. Soc.
1887. Bayeux Tapestry. Scribner's Magazine.
1888. A Liberal Education. Atlantic Monthly.
1888. The United States, their Political Struggles and Relations with Europe. Nar. and Crit. Hist. of America.
1889. Life of Benvenuto Cellini. Scribner's Magazine.
1892. The Eve of the French Revolution.
1893. Clothes Historically Considered. Scribner's Magazine.
1893. Memoir of Lord Tennyson. Proc. Amer. Acad.

1895. HENRY W. HAYNES.

ROBERT CHARLES WINTHROP.

THE HON. ROBERT CHARLES WINTHROP died in Boston on the 16th of November, 1894, at the age of eighty-five years and six months, having been born on the 12th of May, 1809. He was the son of the Hon. Thomas Lindall and Elizabeth (Temple) Winthrop, and a descendant of Governor John Winthrop, founder of the Massachusetts Bay Colony. Between this illustrious ancestor and himself were interposed five generations. His father, Thomas Lindall Winthrop, was for many years Lieutenant Governor of Massachusetts, and also President of the Massachusetts Historical Society; he was universally esteemed as a man of courtly manners, social disposition, and stainless character, rendering much more valuable service to the community than many men of greater intellectual prominence. Robert C. Winthrop was educated at the Boston Latin School and at Harvard College, graduating with distinction in the class of 1828. The social position of his parents at once introduced him to the most cultivated circles in Boston, and he was conspicuous throughout his life for the strictest devotion to all social duties. He always took keen interest in the militia of the State, as a member and commander of Company A of the First Regiment M. V. M., otherwise the Boston Light Infantry, or "Tigers," and was afterwards an Aide-de-Camp on the staff of Governor Everett.

Mr. Winthrop was admitted to the bar, and studied for a time in the office of the Hon. Daniel Webster. But his attention was early attracted to politics. At the period of his entering college the so called "era of good feeling," which had culminated in the almost unopposed re-election of President Monroe, had come to a violent end in the contest of 1824. Mr. Winthrop's college course nearly coincided with the Presidency of John Quincy Adams, and, as he was beginning active life, a new political party was forming itself, composed partly of old Federalists and partly of such Democrats as had supported Mr. Adams against Crawford, Jackson, and Clay. This party was for a short time dominated by the "Antimasons," a singular association of those who distrusted the political and moral tendencies of secret societies. It early, however, assumed the name of National Republicans, and later settled down as the Whig party. To this party Mr. Winthrop was devotedly attached for the twenty odd years that it had any existence; not merely its favorite candidate for State and national offices, but its untiring organizer, alert every day and every hour to extend its influence and deepen its hold upon the people. He was a popular speaker at all its conventions, and a certain fighting element in his nature, which could use the weapons of fun and sarcasm as well as of argument and pathos, cannot be understood without reading his speeches delivered on these political occasions.

Mr. Winthrop entered the General Court of Massachusetts as a Representative when he was but twenty-five years old, and served in that capacity for five terms, for three of which he was Speaker. In 1840 he was elected to the House of Representatives of the United States, and represented the Boston district in five Congresses. In his fourth term, he was elected Speaker of the Thirtieth Congress. It was during his occupancy of the chair that the venerable John Quincy Adams, rising to address the house, was stricken down at his place, and, being carried into the Speaker's private room, died on the 23d of February, 1848.

It had been Mr. Winthrop's intention to close his career as a Representative with this Congress, but he yielded to the solicitations of his friends to sit for another term. He was of course the Whig candidate for Speaker; but after a contest of unprecedented duration. in which the bitterest partisans, both from the North and the South, united to make any election by a majority impossible, he was defeated by Howell Cobb of Georgia, who received a plurality of two votes.

In 1850, Mr. Webster having resigned his seat in the Senate to enter President Fillmore's Cabinet, Mr. Winthrop was nominated by Governor Briggs to hold the Senatorship till the legislature could meet. This body, on its assembling, was controlled by the "Coalition" of Democrats and Free-Soilers, who elected Robert Rantoul, Jr. Senator for the very few weeks of the Senatorial term then remaining, and chose Charles Sumner for six years.

In 1851 Mr. Winthrop was the Whig candidate for Governor of Massachusetts; but, as the law then stood, an absolute majority was required for a popular election, and, failing that, the Governor was chosen by the newly elected legislature. Here again the Coalition triumphed, no candidate having a majority of the popular vote, though Mr. Winthrop had by far the largest number; and the legislature elected George S. Boutwell.

Thus ended Mr. Winthrop's political service, which had reflected the highest honor on his name, his State and his person. He was a conservative in the truest and highest sense, deeply attached to his country and her traditions, suspicious of everything which tended to break up directly or insidiously the flourishing fabric which had been constructed with such amazing rapidity in the generation that immediately succeeded the misery of Mr. Madison's war, but eager for everything which could promote that wonderful development peacefully and honorably. Those who have been trained to believe that his political conduct showed a lack of moral courage would do well to read the debates on the annexation of Texas and the Mexican war, in which he gave voice completely and convincingly to the highest moral sentiment of Massachusetts. If the present laws of election had been in force at the time he was defeated as candidate for Governor, he would have been declared elected to that post, and probably had no difficulty in securing several re-elections. He was a national patriot, who would not for a score of Senatorships have renounced what he considered his duty to his whole country in submission to any sectional feeling.

Particular attention should be drawn to his services as Speaker, both in Boston and in Washington. It may be confidently asserted that no occupant of those chairs ever discharged his duty with greater dignity, courtesy, and understanding of its minutest details. That he was entirely impartial is proved by the fact that fifteen of the very bitterest and most irreconcilable extremists, equally divided between North and South, voted to strike out that word from the vote of thanks to him.

For the last half of Mr. Winthrop's life he occupied what is called a private station. He had, indeed, allowed his name to head the Democratic electoral ticket in 1864, with no idea that he could be chosen. But there have been very few men in any country, or at any period, who have discharged so faithfully, usefully, and acceptably such multifarious public duties. The record of them is to be found in the second, third, and fourth volumes of his public addresses, the first being chiefly occupied with those of a political character. These addresses range over a great variety of subjects, charitable, literary, historical, commemorative. One may select, as specially worthy to be studied, those on laying the corner stone of the Washington Monument in 1848, on the dedication of the statue of Franklin in 1856, and on the centennial anniversary of the surrender of Yorktown in 1881. But, whatever the occasion, Mr. Winthrop was sure to invest it with a richness of historical record, a tenderness of personal reminiscence, an appropriateness of local and contemporary illustration, and a soundness of social philosophy, all conveyed in faultless English, to which there are few parallels. The sense of order and propriety was extremely conspicuous in all he did; he possessed a keen sense of humor, and, as has been stated, in his earlier years an entire willingness to fight; but he objected to engaging in any but clean warfare, and for many years before his death dealt only with such things as make for peace.

The expression used above, that the record of his public service may be found in his speeches, should be corrected; he was the soul of many most important organizations, where his instinct and experience in transacting society business was of incalculable value. Of the many charitable, religious, and antiquarian bodies that looked to him as their guiding spirit, two, the Massachusetts Historical Society and the Peabody Education Fund, were his chosen spheres of constant action. To the Collections of the former he contributed precious stores from his family papers; and his "Life and Letters of John Winthrop" is a most important contribution to our national biography. The various donations of the late George Peabody were made very largely from Mr. Winthrop's direct suggestion; and he threw himself heart and soul into the work of making the Peabody Education Fund immediately and extensively useful for the most pressing need of the Southern States. From this cause his name undoubtedly will be honored and loved hereafter by whole communities, who never heard of the Arbella's voyage or the Antinomian Controversy, — the transit of Venus or the Speakership election.

Mr. Winthrop was chosen a Fellow of this Academy on the 8th of August, 1849, and between 1858 and 1881 he served upwards of twenty years as Counsellor. In 1879 he was appointed Chairman of the "Centennial Committee," and in that capacity was called upon at twenty-four hours' notice to deliver the principal address at the celebration of the one hundredth anniversary of the foundation of the Academy, on the 26th of May, 1880, when it became evident that our

President, the Hon. Charles F. Adams, was too seriously affected in health to fulfil that duty. Impossible as it was in so brief a time for the orator to do justice to himself or the occasion, he gave an eminently graceful and appropriate discourse.

Mr. Winthrop was twice married, and three children survive him. The memory of his character and services is among the precious possessions of this century in Massachusetts.

1895. WILLIAM EVERETT.

ASSOCIATE FELLOWS.

WILLIAM HOLMES CHAMBERS BARTLETT.

WILLIAM HOLMES CHAMBERS BARTLETT, for many years Professor of Natural and Experimental Philosophy in the Military Academy at West Point, contributed as much as any man to impress upon that institution its well known character. As a scientist, he was one of the first to base a system of physics on the principle of the conservation of energy; as a teacher, he was so clear and logical that he made the most complicated laws of physics and astronomy embraced in his course of instruction appear to be self-evident truths. His genial manner and personal interest in his pupils will ever be remembered with gratitude, and his magnetic influence helped to unite the officers of the army and attach them to the Union at a time when so many were tempted to join their native States.

He was born in Lancaster, Pennsylvania, in September, 1804, but his parents moved to St. Louis, Missouri, while he was yet an infant. He was appointed a Cadet at the Military Academy in 1822, graduated at the head of his class in 1826, and promoted to the rank of Second Lieutenant of Engineers. He served at the Military Academy as Assistant Professor of Engineering from 1827 to 1829; as Assistant Engineer in the construction of Fortress Monroe, Virginia, in 1828, and of Fort Adams, Newport, Rhode Island, from 1829 to 1832; as Assistant to the Chief of Engineers at Washington, from 1832 to 1834; as Acting Professor of Natural and Experimental Philosophy from 1834 to 1836; and as full Professor from 1836 to 1871, when, on his own application, he was retired from the active list for forty years of continuous service. Since his retirement he has been Actuary of the Mutual Life Insurance Company of New York. He died at Yonkers, New York, February 11, 1893.

In 1829 he was married to Harriet Whitehouse, of Newport, Rhode Island. Of eight children, three sons and two daughters survive him. His eldest daughter was the wife of General J. M. Schofield, now in command of the army, and his family has always been identified with the army and navy.

In 1837 the degree of A. M. was conferred on him by the College of New Jersey, at Princeton, and in 1847 that of LL. D. by Geneva College, New York. He has been a corporator of the National Academy since 1863, an Associate Fellow of the American Academy since 1845, and a member of the Philosophical Society of Philadelphia since 1840, and also of other societies.

He was the author of a Treatise on Optics, 1839; Synthetic Mechanics, 1850–58; Acoustics and Optics, 1852–59; Analytical Mechanics, 1853–59; Special Astronomy, 1855–58; — all designed for the use of the cadets of the United States Military Academy. He was also the author of "Mortuary Experience" of the Mutual Life Insurance Company of New York from 1843 to 1874; and of official reports and contributions to the publications of scientific societies.

His Analytical Mechanics passed through nine editions, and was used extensively throughout the country. In his Preface he says: "The design of the author is to give to the classes committed to his instruction in the Military Academy what has appeared to him a proper elementary basis for a systematic study of the laws of nature. The subject is the action of force upon bodies, — the source of all physical phenomena, — and of which the sole and sufficient foundation is the comprehensive fact, that all action is ever accompanied by an equal, contrary, and simultaneous reaction. Neither can have precedence of the other in point of time, and from this comes that character of permanence in the midst of endless variety apparent in the order of nature. A mathematical formula which shall express the laws of this antagonism will contain the whole subject, and whatever of specialty may mark our perceptions of a particular instance will be found to have its origin in corresponding peculiarities of physical condition, distance, place, and time, which are the elements of this formula. Its discussion constitutes the study of Mechanics. All phenomena in which bodies have a part are its legitimate subjects, and no form of matter under extraneous influences is exempt from its scrutiny. Astronomy, terrestrial physics, and chemistry are but its specialties; it classifies all of human knowledge that relates to inert matter into groups of phenomena, of which the rationale is in a common principle; and in the hands of those gifted with the priceless boon of a copious mathematics, it is a key to external nature." Twenty years later, in the ninth edition of the same work, in referring to this formula, he says: "That formula was no other than the simple analytical expression of what is now generally called the law of the conservation of energy, which has since revolutionized physical science in nearly all its branches, and which at that time was but little developed or accepted. It is believed that this not only was the first, but that it even still is the only treatise on Analytical Mechanics in which all the phenomena are presented as mere consequences of that single law."

His report of an inspection of the European Observatories, made in 1840, gave an impulse to astronomical work which resulted in the establishment of observatories in all parts of the country.

1895. W. R. LIVERMORE.

EZEKIEL GILMAN ROBINSON.

EZEKIEL GILMAN ROBINSON, an Associate Fellow of our Academy since 1885, was born at Attleborough, Massachusetts, on March 23, 1815. It was not his good fortune to begin his life in a literary atmosphere, or to spend any of his earlier days in tumbling about in a library. His early instruction was poor, and what was bad in itself was made worse by reason of frequent changes.

Entering Brown University in 1834, he was during his first year interrupted in his work by sickness, and, discouraged by his manifest inferiority to classmates who had been more thoroughly prepared, he seemed to lose ambition. Later, however, the student's enthusiasm was awakened under Professor H. B. Hackett in Latin, and under President Wayland in ethics. But in addition to the inspiration received from his teachers, he found a strong educational stimulus in the debating society of which he was an enthusiastic and prominent member. In his enthusiastic and successful work in this debating society we discover the prophecy of the Socratic teacher and the great pulpit orator of later days; while in his choice of theme for Commencement, "The Value of Metaphysical Speculations," we detect the mental bias which was followed through scores of years of philosophic study.

After a year spent in post-graduate work he determined to study theology, and entered the Theological Institution at Newton Centre, Massachusetts. Then, according to his own testimony, he "went to work in earnest with a will and a purpose, giving his days to prescribed work, reserving an hour or two for German and associated readings with fellow students, and devoting his evenings to philosophy and literature."

After graduating from Newton in 1842, Mr. Robinson was ordained and settled as pastor of a Baptist church in Norfolk, Virginia. During this pastorate he received leave of absence from his church, in order to serve for the eight months of an academic year as chaplain of the University of Virginia.

After pastoral service of three years at Norfolk and one year at Cambridge, Massachusetts, the call came to leave the pastorate and to devote himself to the instruction of students for the ministry, and he became Professor of Biblical Interpretation in the Western Baptist Theological Institute at Covington, Kentucky. This connection was terminated after two or three years of service, and Mr. Robinson again entered the pastorate in 1850, in the service of the Ninth Street Baptist Church of Cincinnati, Ohio. Here his reputation as a great pulpit orator was firmly established. He became the foremost preacher of the city, and his reputation was rapidly extending throughout the country. But the man was coveted for other positions, and having received an invitation to accept the chair of theology in the recently established Seminary at Rochester, New York, he, after three years of ministerial service, again left the pastorate for the Professor's chair.

Although after leaving Cincinnati Dr. Robinson never re-entered the pastorate, he continued to preach up to the time of his death. He loved the work of the preacher; he honored the preacher's office, and in that office he was conspicuously successful. His sermons in Cincinnati and Rochester on Modern Skepticism, made deep and lasting impression on the intelligent citizens who came in large numbers to hear them; and throughout his life he was an attractive, instructive, and inspiring preacher. His pulpit presence was striking and effective; his conduct of worship was impressive and memorable; but it was in the sermon that his powerful personality came into fullest manifestation. He was pre-eminently an instructive preacher. Not infrequently were his sermons packed with the results of the thinking of months and years. On special occasions he appeared a veritable giant in intellectual power. He chose the extemporaneous method of delivery; but the extemporaneous method did not exempt him from careful preparation. It was only through the most exacting mental discipline and the most patient literary cultivation that he became the consummate master of unwritten discourse that he was. As he said himself, "It is not the naturally fluent man who makes in the end the best extemporaneous speaker."

His sermons in general were characterized by comprehensiveness of thought, by keenness of analysis, by sharp discrimination in definition, by clear, forceful, and elegant diction, by honesty and earnestness of purpose, and on occasion by tremendous power of appeal. One other characteristic of his preaching, which is worthy of special mention, was what might be called his intellectual honesty. His moral honesty was shown, as, shunning all hypocrisy, he preached level with his convictions. His intellectual honesty he illustrated, as, guarding against prejudice, he preached level with his thinking. He thought as earnestly and as far as he could, and very few thought further; but where his thinking stopped, there his sermon stopped also. He did not urge upon the minds of his hearers what had failed to gain the assent of his own thinking mind. He knew but in part, and he was honest enough to prophesy but in part.

In accepting the chair at Rochester in the spring of 1853, Mr. Robinson exchanged the work of the pastor for that of the theological instructor, for which he was admirably fitted, and in which he was pre-eminently successful. As a theologian he was pre-eminently an investigator rather than a systematizer, or, to use his own word, a "systemizer." He believed that investigation must be carried to great lengths before the work of systemization can be satisfactorily performed. He was too logical to be unsystematic; but his critical faculty was always hindering and interfering with the work of construction. If, through his lack of complete system, and by reason of his dominant tendency to emphasize one phase of truth at a time, he sometimes laid himself open to the charge of inconsistency, he at least escaped some of the faults of the systemizers. If his mind was too critical hastily to construct a system, it was too honest to falsify facts or to minify truths.

Dr. Robinson believed in and taught a rational theology. He cared nothing for words except as they gave expression to reality. He was constantly looking through the formula to the fact, and discarding tradition for truth. He revered historic creeds, as statements of belief which have been formed after profound experience, and which signalize the victories and the progress of Christian truth; but he scouted the idea that any divine fact or truth can be exhaustively measured by finite minds, or that there has been or ever can be an ultimate dogma in theology. The Scriptures, as an organic whole, he considered as authoritative; but he reacted from that method of using particular proof texts which prevents men from seeing the forest for the trees. Discarding the rule that reason may guide us in examining the evidences of Divine revelation, but must be scrupulously abjured the moment we come to an examination of the truths which revelation declares, he inquired, "To what does revelation address itself, if not to our reason and our conscience? In the name of reason, for what was reason given us if not to be employed on the highest thoughts and the noblest ends that can engage our attention?"

Again, he believed in and taught a progressive theology. Before the name became familiar, he represented the movement which has since been denominated the New Theology. He was in advance of most of his contemporaries in welcoming the discoveries and paying earnest heed to the teachings of physical science. He was constantly modifying his own views, was quick to detect the way to fresh discovery, and anticipated the modifications which the new revelations of the age have effected in theology. His ablest students affirm that, in the modifications which they have been compelled to make within the last twenty-five years, they have but followed the lines of thought indicated by Dr. Robinson to his students from twenty to forty years ago.

Great as was Dr. Robinson's work as a theologian, his work was still greater as a teacher of theology. The testimony of his pupils is strong, concurrent, enthusiastic, and convincing with regard to his transcendent ability as a teacher. His method was Socratic. By his keen questions he aroused his students from their dogmatic slumbers, by his personal magnetism and strong intellectuality he led them to discover themselves, and quickened them into newness of intellectual life; while the vital themes he presented sank deep into their hearts and were wrought into the very fibres of their moral and religious nature.

This brilliant and eminent success in the chair of theology made Dr. Robinson a marked man in educational circles; and it is not surprising that, when Brown University was looking for some able and progressive man to become her head, she should turn with longing eyes to the eminent teacher at Rochester. Alma Mater extended a call to her brilliant and distinguished son, and he loyally responded, assuming the duties of the Presidency in the fall of 1872.

The college at that time did not hold a very advanced position. In its material and intellectual condition it needed regeneration, and demanded close attention and self-denying effort from the incoming President. To the work which lay before him he consecrated all his powers, under that stern conviction of duty which dominated his life. The requirements of admission were raised, until at one time they were said to be in advance of the requirements in colleges generally; more room was provided in the curriculum for the modern languages and the natural sciences; and, in harmony with the insistent purpose of the President, better equipment was provided for the application of science to the arts.

Towards the latter part of his administration the President renewed and urged more strongly his demand for an enlarged attention to the study of English; presented a plan by which young women might share in the advantages of the University, and succeeded in extending its work so that students might pursue post-graduate studies at their Alma Mater and receive from her the degree of Doctor of Philosophy.

While these changes were effected in the inner life of the college, in the outward condition improvements were made with accelerating rapidity. Indeed, it showed greater material advance during the administration of Dr. Robinson than at any other period of its history. The grounds were greatly improved; the University came to be much better housed and equipped; the educational plant was very greatly extended, while the funds were almost doubled.

As the head of the college, President Robinson had a deep concern for the moral welfare of his students, and if in specific cases of discipline, he was not always happy, the general discipline of the institution during his administration was efficient and wholesome. For if, owing to his natural reserve and his sternness of demeanor, the President was not always able to win the affection and love of the students, he exerted upon them a most wholesome disciplinary influence through the example of industry, high moral purpose, and constant devotion to duty which he himself afforded. Under this inspiring influence the aims of the students were heightened, and the spirit of devotion to study was very greatly increased.

But the work of administration and discipline did not relieve Dr. Robinson from special work in teaching. During his entire administration he was engaged five or six hours a week in teaching. Very few students, perhaps no earnest student, could fail to receive a deep impression from Dr. Robinson's instruction in ethics. The teachings most deeply impressed were the immutability of the moral law, and penalty as a reaction from violated law; the nature, and not simply the will, of the Supreme Being as the ultimate ground of virtue; and conscience as, strictly defined, neither legislative nor prophetic, but rather as the supreme, though not infallible, "moral judiciary of the soul."

His careful efinition was of great benefit in giving to the pupil solid ground on which to stand. The ethical universe remained no longer chaotic, inchoate, an earth without form and void, illumined by light transfused through an omnipresent mist; but, under his teaching, dry land began to appear in the midst of the waters, and sun, moon, and stars shone out as distinct luminaries in the ethical firmament. Students who have continued to prosecute their studies, for instance on the subject of conscience, after being surprised to see how vaguely and without precise definition that term is used even by writers of eminence, have come to feel a deeper gratitude to their college instructor for his sharp definition. They may perhaps think that the definition given was not sufficiently comprehensive; but that definition has risen, amid the haze which seems to enwrap many ethical writers, like the island which Kant saw outlined amid the restless waters, the obscuring mists, and the dissolving phantoms of a wide and stormy ocean.

But no estimate of the teaching would be adequate which failed to take account of the teacher. The man was in his teaching, the living truth was in the man; therefore his teaching did not simply add to the intellectual capital of the pupil, it became an element in that pupil's moral life. In his best moods his class-room was a forge, where, in the fires of his own intense thinking, heated seven times hotter under the blast of free discussion, the cold iron of traditional notion was fused and then taken out, hot and fluent, to be fashioned anew under the hammers of master-workman and apprentice alike; or, to change the figure, that class-room was a palæstra where he who wrestled the best enjoyed the fullest discipline and received the richest reward, as he carried away his "apples of gold in pictures of silver."

The preacher, the administrator, the teacher, demands our admiration; but still more admirable is the man himself. Towering above many in physical stature, he towered also in intellectual power and moral character. On the physical side of his nature he was endowed with a striking personal presence, and a wiry well knit bodily frame; but these were only the physical setting of pre-eminent intellectual power.

His paramount mental characteristic was his power of analysis. His mind was a crucible, in which, when heated by the intense fires of his intellectual nature, thoughts were readily resolved into their constituent elements. But he was by no means lacking in synthetic power. This was seen in his well constructed sermons and in the broad generalizations and brilliant inductions of his theology; but the analytic dominated the synthetic, as is evident from the fact that his theology was never thoroughly systemized.

But the moral man is grander than the man of intellect, and Dr. Robinson's moral character demands a higher admiration than his intellectual power. He had his faults; but his aim was high, his motives noble, and his heart sincere. His most prominent moral characteristic was tremendous power of will. The man's whole countenance betokened a dominant, imperious will; but this mighty energy was associated with a stern sense of moral obligation. This will was not prostituted to low ends. It was not self-will. It recognized a law to be obeyed, and it held the man in its grip until he rendered obedience. As in the tremendous energy of will we discover the centrifugal force, so in the high moral ideal we discover the centripetal force, which determined the orbit of his life.

The life which was characterized by this striking combination of tremendous energy of will and high sense of moral obligation also displayed a not unhappy union of pride and humility. Probably no human pride is virtue unalloyed; but there is a pride which savors more of virtue than of vice. Essential manhood is worthy of respect. The Almighty has placed man's head erect upon his shoulders; He has "made him a little lower than God, and has put all things under his feet"; the great moral teacher of the ages inculcates self-respect, as he instructs man to love his neighbor as himself. In the philosophic Christian sense, Dr. Robinson was exceedingly proud. He had abundant self-respect; he had little self-conceit. His pride was akin to the awe with which Kant reflected upon the moral law within, and differed heaven-wide from that Narcissus-like vanity which pines away in admiration of its adventitious and ephemeral beauty.

This pride, however, retained its virtue, and was raised from the level of the Stoic philosophy to the higher elevation of the Christian religion, as it was mated to humility. Humility, with him, was not cringing before one's fellows and asking their pardon for one's existence; it was not an undue depreciation of self; it was rather a just appreciation of another and a worthier, in comparison with whom self seems but little. Dr. Robinson bared his head before the Almighty. He walked humbly before his God.

It was in the closing period of life that the strength and nobility of his character found fullest and most beautiful expression. Although Dr. Robinson was seventy-four years of age when he laid aside his duties as President of Brown University, his work was not yet done. In response to the call of honor and of duty, the stern believer in moral law again took up his burden and pressed on toward the goal. Continuing his intellectual toil, he devoted himself to the work of preaching and lecturing, until he again entered the teacher's chair as Professor of Ethics and Apologetics in the University of Chicago, where he remained until he was removed by death on June 13, 1894. It was in this autumnal season that the peaceable fruits of righteousness most rapidly matured. The character which had been steadily and sturdily growing in early and more mature manhood, blossomed in old age. Sorrows deep and distressing were experienced, but the discipline of sorrow seemed only to beautify the character which the discipline of work had made strong. The nature was mellowed, and the heart which had been so jealously guarded through life now overflowed, and gave freer expression to its deeper feeling. The column had been piled stone upon stone, with severe and unremitting toil, the surface had been chiselled with painstaking diligence and skill, until, as a finishing touch, the lily was carved at the top of the pillar, and strength was crowned with beauty.

His chief literary remains are a translation of Neander's "Planting and Training of the Christian Church," his "Yale Lectures on Preaching," and his "Principles and Practice of Morality," together with shorter articles in magazines, notably in "The Christian Review," of which he was editor from 1859 to 1864. During the last year there issued from the press a limited edition of his "Christian Theology," which is chiefly a republication of his lectures as prepared for the use of his students in Rochester prior to the year 1872, and in the present year have appeared his lectures on "Christian Apologetics."

Dr. Robinson's scholarship was officially recognized by his Alma Mater, which conferred upon him in 1853 the degree of Doctor of Divinity, and in 1872 the degree of Doctor of Laws; and by Harvard University, which conferred on him the degree of Doctor of Laws in 1886.

1895. THOMAS D. ANDERSON.

WILLIAM DWIGHT WHITNEY.

WILLIAM DWIGHT WHITNEY, an Associate Member of the Academy since 1860, was born at Northampton, Massachusetts, on February 9, 1827. His early education he received in his native place. In 1842, at the age of fifteen, he entered the Sophomore Class of Williams College. There he remained during the three following years. While there, though he paid due attention to the required studies of the course, he did not confine himself to them. He had an inborn taste for the natural sciences, and spent no small share of his time in botanical excursions among the fields and wooded hills encompassing the college town. There too and then he began the work of making and mounting the collection of the birds of New England, which he subsequently presented to the Peabody Museum of Yale University.

In 1845 he received his bachelor's degree. In spite of the time he had given to studies outside of the regular curriculum, he had easily maintained the position at the head of his class. At that period he had little thought of what was to be the work of his life, and the bent of his mind was certainly then rather towards the natural sciences than languages. He at first contemplated pursuing the study of medicine, but an accidental illness prevented him from carrying the scheme at once into effect, and when laid aside it was discarded altogether. In the uncertainty attending his future he remained in his native place, and entered as teller the bank of which his father was president. In that position he continued for more than three years. Whitney was by nature a man of method. It was that quality which enabled him to accomplish with apparent ease so many things which lay outside of the special pursuits to which he directed his main attention. But while under any circumstances he would have displayed this characteristic, there can be no question that the business training which he received during this most impressionable period of his life did much to impart additional strength and efficiency to habits which had been implanted by nature. In no sense was the time thus employed wasted. Nor were his business occupations so engrossing that he was prevented from carrying on the pursuits in which he had already taken special interest. He completed his collection of New England birds; he made botanical excursions in the neighborhood of his home; he prosecuted vigorously the study of two or three modern languages. These avocations furnished a by no means unsuitable preparation for the work he was to accomplish in other fields.

Up to this time, as has already been intimated, his interests lay mainly in the direction of the natural sciences. But an event was now about to occur which was destined to change the course of his studies and to determine his whole future. In 1847, his elder brother, Professor J. D. Whitney, had returned from Germany, where he had been devoting himself to the science in which he has become distinguished. Yet while there he had not limited his attention to it, but had given up a good deal of time to language. Among the books he brought back with him was a copy of the second edition of Bopp's Sanscrit Grammar. This work attracted the attention of his younger brother, and aroused a keener interest than he had before felt in any particular subject. In the winter of the following year he began the systematic study of Sanscrit. For him this was the parting of the ways. In June, 1849, indeed, he joined an expedition sent out by the United States government to explore the region about Lake Superior. One of its two directors was his elder brother, and to the future philologist were assigned the barometrical observations, the botany, and the charge of the accounts. But he took with him also this copy of Bopp, and the leisure moments he enjoyed during the expedition were, as far as possible, devoted to the fuller study of that work.

His progress in it at that time definitely decided his career. The study of Sanscrit is a pursuit which in any country has never been specially lucrative; and in the United States at that time there was certainly little to prompt any one to choose it as a profession. Whitney's father, a business man, and naturally anxious for the success of his children, saw this clearly; but he was not disposed to stand in the way of a pursuit upon which his son had set his heart. Accordingly, the latter was allowed to follow his choice. The only instruction in Sanscrit then offered in the United States was at Yale College, where in 1841 Edward E. Salisbury had been created Professor of that tongue and of Arabic. To New Haven, therefore, Whitney repaired in the autumn of 1849, and to the study of Sanscrit he devoted the following year. He had but one fellow student, Hadley, who had been made in 1848 Assistant Professor of Greek, and whose comparatively early death Whitney was always wont to lament as the greatest loss American scholarship had up to that time suffered.

After remaining a year in New Haven he sailed in the autumn of 1850 for Europe. He was absent for three years. Arabic, Persian, Egyptian, and Coptic were attacked by him; but his attention was mainly given to Sanscrit, which he studied at Berlin under Weber, and at Tübingen under Roth. In conjunction with the latter he began the preparation of an edition of the Atharva-Veda, and with this object in view spent some months before his return in Paris, in London, and in Oxford, engaged principally in the collation of Sanscrit manuscripts. He reached America in August, 1853.

In 1854 the chair of Sanscrit and Arabic, held by Professor Salisbury, was at his wish divided. At his suggestion, also, Whitney was called to the newly created separate chair of Sanscrit. It was a position the latter held to his death, though to the title was subsequently added Comparative Philology. In 1856 appeared the text of the first important work in the production of which Whitney bore a part, the *editio princeps* of the Atharva-Veda. It bears upon the title-page his name, and that of his old instructor, Roth; but the subsequent labors bestowed upon this one of the Vedas were by him alone. It was in 1849 that an article of Whitney's had appeared in the August number of the "Bibliotheca Sacra." It was an abridged translation of the once popular treatise *Das Alte Indien* of the orientalist Van Bohlen. This was the beginning of a long career of literary activity, the records of which can be found in the journals of Europe and America, in the proceedings of learned societies, and in independent publications. The list of his published productions numbers about one hundred and fifty titles. They range all the way from comparatively brief pieces, which appeared in weekly periodicals, to works involving immense time and labor in their preparation, such as the text and translation of and notes on the "Taittirīya-Prātiçākhya," and its commentary, the "Tribhāshyaratna," for which the Bopp prize was awarded him by the Berlin Academy of Sciences. A large part of what he produced in his special field of investigation made its appearance in the successive volumes of the "Journals and Proceedings of the American Oriental Society," though it was by no means confined to that publication. In particular should be mentioned his Sanscrit Grammar, and his contributions to the great seven-volumed Sanscrit-German Lexicon, published by the Imperial Academy of Sciences of St. Petersburg. Of this latter work he was one of the four collaborators who faithfully assisted the editors, Böhtlingk and Roth, during the twenty-three years taken up with its progress through the press. Besides these purely technical productions he contributed to a number of periodicals essays on various Oriental and linguistic topics of more or less general interest. These were collected by him and published in two volumes in 1873 and 1874; but the work of his that up to that time appealed most to the public of educated men was his treatise on the principles of linguistic science, which came out in 1867 under the title of "Language and the Study of Language." An outline of this same science, covering essentially the same ground as the preceding work, was published in 1875 in the International Scientific Series, under the title of "The Life and Growth of Language." It was then the only popular and at the same time scientific exposition of the subject which can be found in any tongue, and such it has remained to the present day.

Whitney took up his residence in New Haven in 1854, and with the exception of occasional visits abroad, New Haven remained his abiding place until his death. In 1869 he was called to Harvard University, and, had it not been for the prompt gift by Professor Salisbury of the sum needed to endow fully his chair at Yale, he would have felt bound, in justice to his family, to accept the similar chair in the sister institution, now so ably filled by his pupil, Professor Lanman. In 1856 he had been married to Elizabeth Wooster Baldwin, the daughter of Roger Sherman Baldwin, once Governor of and United States Senator from Connecticut. The union was a peculiarly happy and helpful one, and the assistance he received from the members of his family, as time went on, was an important agency in enabling him to accomplish so much in so many different ways. Three times he visited Europe, and once remained there fifteen months, engaged in the preparation of his Sanscrit Grammar. In fact, all his journeys abroad had as one of their principal objects the completion or more successful prosecution of some work upon which he was at the time employed.

The pay of his professorship was at first very small, and in the college year of 1856–57 he was appointed Instructor in German in the Academic Department. His duties, however, were limited to the third term and to the Junior Class. In the following year French was added to the then narrow list of electives, and in that tongue also he was called upon to impart instruction. This duty of teaching these two languages in the Academic Department Whitney continued to discharge until 1867. Then he turned over this work to the Professor of Modern Languages, for instruction in which a special chair had been created three years before. After 1871, however, he gave an elective in linguistics to the students of the classical course.

It was while he was teaching French and German in the Academic Department that I first came under his instruction, and made his personal acquaintance. Though then myself a mere boy, I could not fail to be struck with the earnestness and thoroughness which he brought to the performance of duties that most men of his grade would have deemed the veriest drudgery; with the breadth and accuracy of his knowledge, and the lofty standard of scholarship he set before us all; but perhaps at that time more than with anything else, with the patience which no indifference ever discouraged, no thoughtlessness ever irritated, and no stupidity ever tired. All these feelings were intensified when several years later I came to be his colleague and personal friend.

In 1861, while still an instructor in modern languages in the Academic Department, he was called upon to perform the same duties in the Sheffield Scientific School, then a small part of the University, but about to enter upon a rapid course of prosperity. With it he speedily became identified in spirit, and his instruction in it did not cease until 1886, when the disease manifested itself which eventually struck him down. To the School his connection was of enduring benefit. He was in the fullest sympathy with its objects and aims, was profoundly interested in its success, and was unremitting in his efforts for its advancement. It was largely, perhaps mainly, due to his influence, that this department of the University never degenerated into a merely technical institution; that in it the study of language and literature always occupied a position of equal prominence and honor with the purely special subjects which it set out primarily to teach. While the School was small and the number of students few, he gave instruction both in French and German. But it was not many years before its rapid growth compelled him to confine himself to one of these two subjects. From 1869 to 1872, he taught German alone; after the latter year till 1886, French alone. It is, however, to be added, that during the whole period of his connection with the School he gave instruction in linguistics to the students of one of the special courses.

He received then and subsequently a good deal of sympathy for the time thus spent in elementary instruction, and to many it will seem a waste of power to have so employed it. But it was largely his own choice. He kept up the practice long after the necessity which led him at first to assume it had passed away. Nor, in fact, did it seriously encroach upon his leisure. Whitney, as I have observed previously, was a man of method, and the hours of his day were so regulated and disposed as to secure the largest results with the least friction. A single incident will illustrate how carefully his time was measured. French and German were compulsory studies upon all students, no matter what their special courses. In order to get them out of the way, the first hour of the morning was given up to recitations in these two languages. This had been from eight to nine; but at one of the few meetings of the Governing Board of the Sheffield Scientific School, from which Whitney was absent, it was decided to change the time, so that henceforth it should be from half-past eight to half-past nine. But to this he felt obliged to refuse his consent. The hour from eight to nine he was willing to give up to this instruction, but nothing more. There was accordingly no other course left for the Board, unwilling to lose his services, than to rescind promptly its previous action.

The relation, furthermore, which he held to the Scientific School, he felt was of advantage to himself in many ways. He has more than once assured me that his connection with it, his intimate acquaintance with the spirit which pervaded it, his knowledge of the work accomplished by it, had done more than any other one thing to broaden his mind on the whole subject of intellectual training; to dispel from it the notion that there was but one kind of education in the world; to free it, in particular, from the illiberality which, in the case of some, is the most conspicuous result of an exclusive devotion to what they designate as liberal studies. Another incidental result of this connection with the School was that it led to the preparation of a series of excellent text-books. These have played a most important part in putting the instruction in modern languages on a higher and more scientific plane than it had ever before enjoyed in this, or for that matter in any English-speaking country. The list of these is somewhat remarkable for one who accomplished so much in other fields. In 1869 appeared his German Grammar, in 1870 the corresponding German Reader, in 1877 his German-English Dictionary, in the same year his English Grammar, and in 1886 his French Grammar. All these were worked up with his usual thoroughness, and exhibit the latest results of linguistic investigation. Had they taken his time from his special studies, their preparation might have been a matter of regret. As it was, it is nothing but a subject of congratulation.

The preparation of the French Grammar occupied a portion of the earlier months of 1886. It was then that Whitney felt at times a pain in his arms, occasionally so severe that he would be under the necessity of keeping them for a while folded. It was naturally attributed to rheumatism. The summer of that year was spent in Kittery, Maine, and while there these pains extended to the chest. Still they occasioned no serious alarm, and the physician whom he consulted did not venture to speak positively as to their cause. It was not until his return to New Haven in the autumn that the increase in the frequency and violence of these symptoms led him, at the suggestion of his family physician, to seek the advice of a specialist. In October he went to New York and consulted Dr. Loomis. That practitioner, after a careful examination, felt compelled to warn him that the situation was exceedingly grave; that in fact the heart was so seriously affected that the chances were heavily against his living more than six weeks; and that, if his life should be protracted beyond that period, it could be done only by the immediate cessation of all work, and by steadily conforming to a most exacting regimen as regards labor and diet, which few are found willing or sufficiently self-controlled to maintain for any length of time.

In a man whose life had been spent in study and investigation, and who had found in them supremest pleasure, this unexpected revelation of his physical condition was necessarily a severe shock. He was in the midst of work well advanced towards completion. He had formed projects and made engagements for the future. His intellectual force was unabated. It was hard for him to stop suddenly short, and play the part of a confirmed invalid. But the situation had been too clearly pointed out by the physician for him to doubt the correctness of the diagnosis. He bore the blow, however, with the same quiet fortitude with which he had met the various trials of a life in which he had never shirked a duty however distasteful, or shrunk from a task however irksome or onerous. Though hardly hoping to survive the allotted six weeks, he set to work to fight for life on the lines laid down for him with the same calmness and courage with which he would have attacked a delicate and difficult problem of scholastic investigation. For the time being all work was laid aside. He conformed in the minutest detail to the strict regimen which had been imposed. Every effort was bent towards the restoration, so far as was possible, of health. The task was made as easy for him as it could be by the members of his family, all of whom devoted themselves with a single eye to alleviating as much as lay in their power the monotony of this enforced idleness, and to scanning with jealous watchfulness the slightest sign of approaching danger. Yet, in spite of all that ardent affection could do and did do, it was necessarily a grievous burden. Still it was a burden uncomplainingly borne. In time, too, it was lightened. The self-restraint he exercised, the rigid rule he imposed upon himself, met with a partial reward. Though it could not avert the sentence of death which had been pronounced upon him, it was sufficient to suspend for several years its execution. When six months after Dr. Loomis again saw his patient, he made no attempt to conceal his astonishment at the improvement that had been made. The necessity for the most rigid adherence to the rules that had been laid down for his guidance was indeed as pressing as ever; but, with these closely observed, it was reasonable to believe that there was still a chance for him to accomplish much which it had been in his mind to undertake.

From this point on follows a period in Whitney's life of quiet heroism, and. considering the situation he was in, of wonderful achievement. During all those years, in which I saw him not unfrequently, I never knew him to utter the slightest complaint about the calamity which had unexpectedly fallen upon him in the fulness of his strength. He preserved the same cheerful composure which had characterized him in the days of his health and vigor. He gradually and cautiously took up much of the work which he had been obliged to lay aside. He resumed his instruction in his special department, though his classes were now obliged to meet him in his own home. In fact, not a single duty remained unfulfilled which it was in his power to accomplish. Moreover, he carried on to conclusion several undertakings in which he had been concerned, and in a few instances projected others. In particular, during those years he went through the necessary drudgery of reading twice over all the proofs of the Century Dictionary, of which he was editor in chief, and of carrying on a correspondence, which may be fairly called immense, with its numerous sub-editors and contributors; he revised his Sanscrit Grammar, originally published in 1879; and when he died, he was at work upon the second volume of the Atharva-Veda, containing commentary and translation, which had been promised forty years before. As time went on, indeed, his health seemed to improve. It is possible that renewed strength gave renewed confidence, and that he was at last led to venture further than his frail physical condition could endure. These are considerations which are sure to present themselves to those who live to lament him. But it was inevitable that the stroke should fall sooner or later, and against it no precautions could long prevail. In the latter part of May, 1894, his disease assumed an acute and painful form; on the morning of Thursday, the 7th of June, he died.

Of the value of Whitney's services in the special fields of investigation to which he devoted his life, others can speak and have spoken with an authority to which it would be presumption in me to lay the slightest claim. Yet it is certain that down to the very close of his career his eminence was undisputed. He lived long enough to see the studies which he had been almost the first in this country to take up pursued enthusiastically by hundreds. But the progress of their investigations, the results of their researches, never once shook his commanding position. To the younger linguistic scholars of the country he remained to the last the master. He was the friend to whom, whether students of his or not, they came for advice and encouragement. He was the leader to whom they looked for guidance. He had undoubtedly here his critics and opponents, but they were never found among the men who stood highest in the department of study in which he had been with us the great pioneer. They were almost invariably the mere echoers of the views of his adversaries across the ocean, and not only were they never very numerous, they were never very effective.

But without expressing any opinion upon the comparative value of the work he accomplished, there were certain characteristics distinguishing his scholarship which can be read and known of all men, and which naturally forced themselves upon the attention of any one whose relations to him personally were close enough to render it frequently necessary to seek his advice and to ask his direction. One of these was his thorough intellectual independence. No one was ever less influenced than he by the authority of great names. No one was ever less affected by the general acceptation of plausible theories. He came to the examination of every subject, not with any desire either to adopt or to attack the conclusions of others, but to study it for himself in the light of truth. It was accordingly his good fortune to see views, which he had unsparingly censured while they were widely held, abandoned by the vast body of scholars. The controversies in which he became engaged were, indeed, largely due to his severe and almost contemptuous criticism of doctrines which had little to show in their favor but superficial plausibility, though often presented in a captivating form. His unhesitating rejection of theories which had wide vogue, his exposure of the fallacies of men with wide reputations, distressed always, and often irritated, that body of partisans attaching themselves to noted names, who, while never possessing the courage of their own convictions, display invariably the most unreasoning and undaunted hardihood in upholding the convictions of others.

Joined with this intellectual independence was his thorough intellectual sanity, if it be not more correct to say that the former was the result of the latter. It is, at any rate, the one quality which will give the greatest stability to the work he accomplished. The advance of scholarship necessarily causes many previously accepted beliefs to be reviewed, many statements to be modified, many received theories to be exploded. It not unfrequently happens that the individual himself lives to see the views he had imposed upon the world set aside as a result of the fuller and clearer light furnished by later investigations. From this too common calamity Whitney has been saved by the sanity of his judgment. There are few scholars who have been called upon to retract, or even modify, so little as he by the advance of knowledge. From this cause his reputation never had to suffer during his life, and, so far as the future can be foreseen, it is little likely to suffer in the years to come.

There are other characteristics of his to which it is not within the limits of the present notice to make more than a passing reference. It is enough to say, in general terms, that those who knew him best esteemed him most. The affectionate regard in which he always continued to be held by the men once brought into close communion with him by the nature of their special studies was due full as much to the respect inspired by his moral qualities as by those purely intellectual. His sincerity, his disinterestedness, his unflinching devotion to duty, could not fail to impress profoundly all with whom he came into constant contact. Speaking for myself personally, I may be permitted to say, in conclusion, after the intimate associations of twenty-five years, that never have I known a man more unselfish in his dealings with others, more loyal to his friends, more genuine in profession, and more upright in every relation of life than he, who held unchallenged during the whole of his career the position of foremost of American philologists.

1895. THOMAS R. LOUNSBURY.

FOREIGN HONORARY MEMBERS.

CHARLES EDOUARD BROWN-SÉQUARD.

CHARLES EDOUARD BROWN-SÉQUARD* was born at Port Louis, on the island of Mauritius, April 8, 1817, and died at Paris, April 2, 1894. His father was an American sea-captain, and his mother, Madame Séquard, was a native of Provence. Left without resources by her husband's death just before the birth of her child, she managed to support herself and him by her needle, and to give him a care and training which gained her his deep love and devotion, and doubtless fostered the affectionate and domestic traits of his disposition which characterized him throughout his life. The extraordinary industry and singleness of purpose which he afterwards showed must have had their root in fine inborn qualities of mind, but his early simple life, with its traditions of hard work and self-reliance, was a good school for virtues of this order.

As a young man, and while supporting himself as agent for a large colonial store, he is said to have tried his hand with local success at polite letters, and soon afterwards to have made his way with his mother to Paris, as an aspirant for literary fame, following in this respect also in the footsteps of his great predecessor in the Chair of Physiology, Claude Bernard.

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* For many interesting facts relating to his life and works, see an address by Eugene Dupuy, published in the Transactions of the Société de Biologie, 1894, which is my authority for most of the data here given.

But he was quickly disillusioned, and, gathering fresh courage, began to prepare himself for the practice of medicine. The next few years covered a period of extreme poverty, in spite of which he dared to devote himself to physiology, though there seemed to be no prospect of support or advancement in its pursuit, and then began that long course of tenacious, unflagging labor in scientific fields which was checked only by his death.

Even the wandering life he led — for he crossed the ocean innumerable times, and planned at different periods to make a home for himself in various cities of Europe and America — did not for a moment arrest his labors or his productiveness, or cause him even to change materially his hours or methods of work. He was in the habit, from the period of his student years throughout the rest of his life, of going to bed at eight o'clock in the evening and rising at two in the morning, in order to have time for uninterrupted work, and even when journeying by land or sea he continued to study and to write. His whole mental attitude was characterized by an eagerness and intensity which made a moment's conversation with him seem like a memorable event. It may be questioned whether his judgment might not have been calmer, and his sense of proportion more just, if the fire of his energy had burned less fiercely; but it is doubtless true that the brilliancy of his scientific imagination, which, next to his tireless industry, was his most characteristic trait, was kept at a glowing heat by this flame.

His first scientific communication of consequence was his graduation thesis, on the "Sensory Tracts in the Spinal Cord," presented in 1846, and the investigations which he made with regard to this matter, both at this time and subsequently, were among the most important of his scientific life. In 1848 he took part in founding the Société de Biologie, and up to the time of his death he remained one of its most active members. In 1852 he embarked in a sailing vessel for New York, and, having utilized the voyage in studying English, he at once began to teach experimental physiology in the medical schools of New York, Philadelphia, and Boston, at the same time writing papers in the medical journals and eking out his small income by teaching French and by practising obstetrics. In 1854 he returned to Mauritius, and during the epidemic of cholera which shortly followed he was put in charge of the hospital. In 1855 he was made Professor of Physiology at the University of Virginia, in Richmond, but his life there was not congenial. An ardent republican, and with the scenes of the *coup d'état* of 1852, in which he had himself borne arms, still fresh in his mind, the contact with Negro slavery impressed him very unpleasantly, and in 1856 he returned to Paris and established a laboratory with his friend Robin. His researches, and especially those relating to the spinal cord and to epilepsy, had by this time made him famous, and he was welcomed as a lecturer in the Universities of England, Scotland and Ireland, which he visited in the course of the next year. In 1858 he began the publication of his "Journal de la Physiologie de l'Homme et des Animaux." He next went to London, where he was made Physician to the National Hospital for Epileptics and Paralytics, and became busy with a large consulting practice; but in 1863 he again broke loose, and came to establish himself in Boston, the home of his first wife, whom he had married on his earlier visit. In 1864 he was made Professor of Physiology and Pathology of the Nervous System in the Harvard Medical School. The loss of his wife, in 1867, determined him to change his plans and return to Europe. In 1868 he founded the "Archives de Physiologie," in company with Charcot and Vulpian. By 1872 he had however again crossed the sea, intending to establish himself in New York, which was the home of the lady who became his second wife, and he at once began together with Dr. E. C. Seguin to edit the "Archives of Scientific and Practical Medicine," which had a brief but creditable existence. The early death of his second wife again broke up his home, and he returned to Europe once more. Within a few years he married for the third time, and had agreed to accept a professorship at Geneva, when the death of Claude Bernard, in 1873, brought him a call to the Chair of Experimental Medicine at the Ecole de Médecine (1878), and this position he held for the remaining sixteen years of his life. His wife, to whom he had been deeply attached, died in 1894, and he survived her only a few months. He worked to the last, and had taken an active share in the preparation of the issue of his journal, the "Archives de Physiologie," which appeared shortly after his death.

Brown-Séquard was the only person whose name appears successively in the three divisions of the American Academy. He was elected a Fellow May 28, 1867, an Associate Fellow May 27, 1873, and a Foreign Honorary Member February 9, 1881.

This is not the place for a critical estimate of Brown-Séquard's work, or an enumeration of his communications. The works by which he will be longest remembered are, perhaps, first, the investigations already referred to with regard to the sensory tracts in the spinal cord; secondly, his insistence on the complex nature of the cerebral functions, and the interaction of one part on another, leading to the phenomena of inhibition and reinforcement; thirdly, his studies on experimental epilepsy; fourthly, his observation that many of the organs of the body, such as the suprarenal capsules and other glands, both ductless and secretive, exercise an important influence on the nutrition of the body through the substances which they pour into the blood. These are all still living problems, and the work which he did on the last of them, though it has led to much adverse criticism, partly just, partly unjust, has borne and will bear practical fruit.

It is true that in collecting materials for the support of the conclusions which he reached he sometimes showed a lack of critical judgment which carried him too far, and impaired the weight of his authority in the eyes of many persons who were not in a position to know the real merit of his work, and to select the grain from the chaff. It is likewise true, however, that his researches gave birth to a splendid array of observations and generalizations, for which his name will be gratefully remembered by every sincere student of physiology.

His friend and co-worker Gley says of him, "Brown-Séquard was one of the greatest discoverers of facts that the world has ever seen."

1895. JAMES JACKSON PUTNAM.

HERMANN LUDWIG FERDINAND VON HELMHOLTZ.

HERMANN LUDWIG FERDINAND VON HELMHOLTZ, one of the most illustrious of European *savants* and one of the most distinguished of the Foreign Honorary Members of the American Academy of Arts and Sciences, was born at Potsdam, Prussia, on August 31, 1821.

Admitted at the age of seventeen to the Royal Military School at Berlin, he became Assistant Surgeon at La Charité Hospital, and later, as full Military Surgeon, was stationed at Potsdam. But after four years of service he relinquished the practice of medicine to enter upon congenial pursuits in extended and accurate mathematical and physiological researches, and in untiring investigations of various intricate questions in physics and optics.

One of the earliest of his published scientific papers, "On the Conservation of Force," gave him at once an acknowledged rank as *facile princeps* among the chief investigators in natural science. This was accompanied by other notable contributions; especially those on "The Nature of Putrefaction and of Fermentation," published in 1843; "On Animal Heat"; and on "The Consumption of Tissue during Muscular Action," in which was considered the question whether the living body gives off as much heat as is produced by the combustion and change of the food it takes in.

In 1849, Helmholtz became Professor of Physiology in the University of Königsberg, where he made notable investigations on "The Rapidity of Propagation of Nerve Excitation." By ingenious methods, of his own devising, for measuring extremely small differences of time, he was enabled to demonstrate that thought is not instantaneous, that it takes a definite period for us to become conscious of a fact, and that a certain measurable time elapses between the willing of a movement and the executing of it.

Helmholtz's original and intricate researches, begun thus early and including every department of physiology and of physics, are a record of amazing originality, acuteness, and industry, largely in new fields. They are especially remarkable for accuracy of observation, and quick discernment in the interpretation of the phenomena investigated. Nothing seemed so insignificant as to escape his notice, and little was so obscure as to defy his explanation.

Among the fruitful practical results of Helmholtz's untiring activities, we do not exaggerate in placing a superlative value upon his invention of the Opthalmoscope, — not only a most precious endowment of science, but as bestowing immeasurable benefits upon the whole human race.

We may well say, with Hasner: "The ophthalmoscope is not only the most valuable boon to ophthalmology, but is also one of the greatest creations of our century. What the telescope is to astronomy, the ophthalmoscope is to ophthalmology. The telescope owed its existence to an accident, but the ophthalmoscope is absolutely the mature offspring of theory, and is therefore a greater ornament than the former, not only to Helmholtz, its originator, but also to the age itself, which has not been here indebted to blind chance for great discoveries, but has known how to deduce them from exact and laborious scientific investigations."

Zehender, himself illustrious as an author and teacher, says of Helmholtz: "For more than two hundred years physiologists and mathematicians earnestly and with great sagacity sought for a solution of the mode in which the eye instantly and involuntarily adapts itself for various distances, near and far. It was reserved for Helmholtz and his collaborator, Cramer, to solve this problem, by proving that an adaptive accommodation is effected by an increase of convexity of the crystalline lens, and principally of its anterior surface, through the agency of the ciliary muscle." The demonstration of these facts, by means of oblique illumination, was in this wise.

In a darkened room, a lamp flame, placed near the eye to be observed at an angle of about 30° from its visual axis, gives, while the eye looks at a distance, to an observer placed at about the same angle at the opposite side of the visual line, three reflected images of the flame: one erect, from the cornea; another, also erect, from the anterior capsule of the crystalline lens; and a third, an inverted and smaller image, from the posterior capsule of the crystalline. If now the observed eye, instead of looking at a distance, accommodates itself for a near object, say at twelve inches, the reflected image from the anterior surface of the lens appears lessened in size and approaches the corneal reflection, — a change which could result only from an increase of convexity of the anterior surface of the crystalline. The inverted image from the posterior capsule of the lens remains practically unchanged in size or position, proving that but slight, if any, change of curvature occurs at this posterior surface of the lens during accommodation for near objects.

Of all proof, we deem ocular evidence the most conclusive. Thanks to Professor von Helmholtz, we possess. in his supreme inquisitor, the opthalmoscope, an interpreter not only capable of revealing and explaining hitherto unknown physiological laws of normal vision, but which also affords clear and positive disclosures of previously unsuspected morbid processes, which, if unarrested, may imperil the most precious of our senses, and our chiefest means of instruction and of enjoyment. More than by any other faculty we live, and move, and learn, and enjoy by that of vision. To our eyes we owe almost everything we have, and are, and hope to become.

Were the revelations of the ophthalmoscope as to pathological and physiological conditions limited to such as affect the eye itself, they would still have an infinite value. But these disclosures have a still wider range, showing, through changes discoverable by its means in the retina and other internal structures of the eye. the advent of yet graver disease in other remote and most important parts of the body, — as, for instance, in the brain or the kidneys, — before the presence of any morbid tendency has been suspected.

Fortunately for science, Helmholtz was pre-eminently an observer and an interpreter; fortunately for science and for himself. he was destined to fill positions, one after another, not only of preferment, but of opportunity. When at an early age, in 1855, four years after his invention of the ophthalmoscope, he was appointed Professor of Anatomy and Physiology at Bonn University; then, three years later he became Professor of Physiology at Heidelberg University. Since 1871 he has been Professor of Physics at Berlin University, and in 1877 he became its Rector, becoming thus a veritable apostle of natural science.

On his election to membership in the French Academy he was hailed as "the foremost naturalist of his age, to whose glory nothing was wanting, but whose admission conferred fame upon the Academy." In 1873, the Copley Medal was awarded to him by the Royal Society of Great Britain.

In 1856, when thirty-five years old, Helmholtz published one of his works, modestly styled by himself a "Handbook of Physiological Optics," but which is a book of more than a thousand pages, — a stupendous monument of his patience, his alert and wise perception, his industry, and his accuracy in a field where not only conditions but functions came to be investigated in the light of new revelations, and where the observer must be a law unto himself.

It was this complete equipment of various knowledge, — in physiology, in physics, in biology, in mathematics, in optics, — joined to powers of quick and accurate perception and judgment, which so greatly enhanced the glory of Germany's and Europe's most illustrious and honored *savant*. It is hoped that the work of the later period of his career may be collected and published, to add yet further contributions to scientific knowledge.

In 1883 an hereditary title of nobility was conferred by the Emperor of Germany upon Helmholtz. In 1891, on his seventieth birthday, a jubilee ovation was tendered to him, where, in response to enthusiastic testimonials of admiration and affection from the German Emperor and other European sovereigns, from the President of the French Republic, from numerous learned societies and the great Universities, the Professor with great emotion referred to his disability of health in his earlier years of childhood, and spoke of his strong inclination, even from that period, for exact and experimental studies, which he had most zealously pursued.

In 1893, Baron von Helmholtz, accompanied by the Baroness, made a brief visit to this country, attending the Pan American

Medical Congress at Washington, and making a trip to the Chicago Exposition and the Western States. Coming afterwards to Boston and to Harvard College, they were greatly pleased with their visit. In paying a visit of respect to them, I remarked, "Professor, we know a hundred fold as much in opthalmology as before you gave us the ophthalmoscope." With a deprecating smile and gesture, he replied, "I was not even a Doctor of Medicine! I was only Professor of Physics at the University! but I set myself this problem. 'To illuminate if I could the interior of the eye,' — and I succeeded!"

Alas! but a few months have passed since the eclipse of that great light which had done so much for those who sit in darkness, for science, and for the world. As the creator of modern opthalmology, substituting by means of the opthalmoscope certainty for surmise, Helmholtz has bestowed an incalculable benefit upon mankind.

1895. H. W. Williams.

At the request of the late Dr. Williams the following account of the original work of Helmholtz was prepared to be added to the biographical notice.

The work of Helmholtz as an investigator seems to have begun while he was studying at Berlin in preparation for the profession of military surgeon. and his first scientific paper was his Promotionsschrift, "De Fabrica Systematis Nervosi Evertebratorum," published in 1842. Helmholtz's knowledge of mathematics, afterwards so profound, appears to have been at this time comparatively slight. His attention was chiefly devoted to physiology, though he was especially interested in physics for its own sake, as well as for the reason that accurate physiological measurements could be made only by persons who were able to devise and to use intelligently physical apparatus.

During most of the interval between 1842, when he became Militär Artz, and 1847, when, through the kind intercession of Alexander von Humboldt, he was honorably discharged from the army, Helmholtz was stationed in his native town of Potsdam, and there, besides carrying on his researches in physiology, some of the results * of which he published, he studied mathematics and physics, with the help of books borrowed from the library of the Gymnasium, to such

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* "Ueber das Wesen der Fäulniss und Gährung," 1843. "Ueber den Stoffverbrauch bei der Muskelaction," 1845. "Die Physiologische Wärme," 1845. "Bericht über die Theorie der Physiologischen Wärmeerscheinungen für 1845." "Ueber die Wärmeentwickelung bei der Muskelaction," 1847.

good purpose that he was soon able to read easily the most abstruse treatises on these subjects, and to write his famous essay, "Ueber die Erhaltung der Kraft," in which the great doctrine of the conservation of energy was first forced upon the attention of physicists. The seven papers which Helmholtz published before he left the army had already (in 1848) given him a high reputation among physiologists, and after a year spent as teacher of anatomy at the Kunstakademie at Berlin, he was called to a Professorship of Physiology and Pathological Anatomy at Königsberg. During the six years which he spent here Helmholtz published about twenty papers, mostly of great importance, and of these almost all, except those on the velocity of propagation of nerve excitation, and on the duration of induced electric currents, had to do with physical or with physiological optics.

These twenty papers, however, do not represent the whole of the work which Helmholtz did at Königsberg beyond his professional duties, for he must have written here the greater part of his "Handbuch der Physiologischen Optik," the first edition of which appeared in 1856. It was by this time clear that Helmholtz had become one of the first of living physicists. Almost every one of his publications, whatever its title, showed his mastery in some branch of physics, and made some contribution to the world's knowledge of the subject.

From Königsberg, Helmholtz went to Bonn, and thence, in 1858, to Heidelberg, where he remained as Professor of Physiology until 1871. While at Bonn and Heidelberg he published forty-three considerable papers, besides his "Lehre von den Tonempfindungen," which appeared in 1862, and which he says in his Preface is fruit of work stretching over eight years,* though of the fourteen publications which he wrote in the six years after he left Königsberg at least five have to do with matter foreign to acoustics and to tone-sensations. One of these was an epoch making paper in mathematical physics, in which it was shown that vortex rings and vortex filaments in perfect fluids under the action of conservative forces are indestructible, and that such rings and filaments apparently attract or repel one another according to the relative signs of their vorticities.

One may get some conception of the catholicity of Helmholtz's tastes and of the extent of his knowledge by reading a list of the subjects of the papers which he wrote at Heidelberg on Physiology, Physical and Physiological Optics, Physical and Physiological Acoustics, the

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* "Indem ich die Früchte achtjähriger Arbeit der Oeffentlichkeit übergebe," etc.

Theory of Perception of Geometrical Truth, the Doctrine of Energy, Hydrodynamics, and Electrodynamics. Towards the end of his stay in Heidelberg, his attention was more and more turned in the direction of physics and away from physiology. He had certainly become the greatest living German physicist, and when Magnus died, in 1871, it was on all sides agreed that he should be called to take the Directorship of the Physical Laboratory of the University at Berlin, and natural that he should accept the position. From this time on by far the larger part of his own experimental work was in the domain of physics, though he suggested and helped on to success the researches in physiology of other experimenters, and when it became necessary to review the whole literature of physiological optics on the occasion of the preparation of a new edition of his Handbuch, he spent much time and energy in studying and in drawing conclusions from the work of others in this field.

Some of the most important of the later contributions of Helmholtz to mathematical and experimental physics are contained in his papers on, —

1. Possible Discontinuities in the Motion of a Frictionless Fluid.
2. The Theory of the Motion of Viscous Fluids.
3. The Thermodynamics of Chemical Processes.
4. The Theoretical and Practical Limits to the Resolving Powers of Microscopes.
5. Electrolytical Processes.
6. The Fundamental Laws of Electrodynamics.
7. Electrical Oscillations and the Nature of Electricity.

In 1888 Helmholtz resigned his place at the head of the Berlin Laboratory in order to take charge of the newly established Reichs-Anstalt at Charlottenburg, and the last years of his life were chiefly spent in organizing the work of this institution.

GASTON, MARQUIS DE SAPORTA.

The Marquis de Saporta was born on July 28th, 1823, and died at the age of seventy-one years on January 26th of the present year, at his residence in Aix-en-Provence.

Since the appearance of his first paper on the Fossil Plants of Provence in 1860, he has been a prominent palæobotanist, and yields to few cultivators of that science in the number, variety, and importance of his memoirs and larger works. His greatest and most important work is that on the Mesozoic Flora of France, to which he added last year a valuable report on the Mesozoic Plants of Portugal. A summary of this last work, in connection more particularly with its bearing on the palæobotany of North America, from the pen of Professor Lester F. Ward, a fellow laborer in the United States, has lately appeared in "Science"; and perhaps with the exception of those of his great rival, Heer of Zurich, who passed away before him, no European works on the botany of the Mesozoic period are more frequently referred to than those of Saporta.

Though a specialist in the floras of the later geological periods, he could enter with enthusiasm into the whole history of the vegetable kingdom, in a manner at once elaborate, careful, and attractive to general readers, and with an enlightened grasp of the succession of plants in time, and of their relations to the various changes of climate and geography in the different periods. This is remarkable in his popular work, "Le Monde des Plantes," which goes over the whole field of geological botany, is written in a clear and vivid style, and illustrated with geological maps and very clever restorations of the forests of different periods.

His memoirs also cover a wide geographical range, as specimens from many regions were submitted to him, and he was always ready, in the kindest and most genial spirit, to give the benefit of his advice and information to his fellow laborers in every part of the world. His work was characterized by much discrimination and care, and by a judicious attention to the geological horizons of the plants he studied, but, like many other palæobotanists, he was occasionally carried away by his enthusiasm, so as to recognize as plants mere imitative markings. This was especially the case in the controversies in which he took part respecting the nature of certain markings on rocks whose algal nature had been maintained by Delgado and others, while to Nathorst, and to palæontologists generally who were familiar with the tracks of animals and the imitative tracings on the surfaces of aqueous deposits, they were of animal or of inorganic origin.

In conjunction with Professor Marion, Saporta published a work on the Evolution of Plants, which forms three volumes of the French International Library of Science. It abounds with curious information of a very suggestive character, but was perhaps too ambitious in the present state of knowledge. This the authors frankly admit, stating, in conclusion, that they can but point out a few landmarks to their successors, "who may decipher the inscriptions of which we can but spell out some letters."

But though an evolutionist, Saporta was by no means an agnostic.

He saw in the grand succession of vegetable forms a great and profound design, related to the inorganic world and its mutations on the one hand, and to the animal kingdom on the other. He sums up this conclusion in his "Le Monde des Plantes" in the following words, which may serve as an example of his style and of his habit of thought in the wider problems of his science: —

"Mais, si l'on remonte de phénomène en phénomène plus haut que les apparences mobiles *et contingentes*, il semble que l'on aboutisse forcément à quelque chose d'entier, d'immuable et de supérieur, qui serait l'expression première et la raison d'être absolu de toute existence, en qui se résumerait la diversité dans l'unité, eternel problème que la science ne saurait résoudre, mais qui se pose de lui-même devant la conscience humaine. Là serait la vraie source de l'idéal religieux; de cette pensée se dégagerait d'une façon lumineuse, cette conception de notre âme à laquelle nous appliquons instinctivement le nom de Dieu."

Saporta was Correspondant de l'Institut de France, a Foreign Member of the Geological Society of London, a Foreign Honorary Member of our Academy since 1885, and an honorary or corresponding member of many other societies on both sides of the Atlantic.

1895. J. William Dawson.

Three Resident Fellows have been returned to the list of Associate Fellows on account of removal from the Commonwealth, and one Associate Fellow has been transferred to the list of Resident Fellows.

The Academy has received an accession of eight Resident Fellows, two Associate Fellows, and five Foreign Honorary Members.

The Roll of the Academy corrected to date includes the names of 195 Fellows, 95 Associate Fellows, and 67 Foreign Honorary Members.

May 9, 1895.

LIST
OF THE
FELLOWS AND FOREIGN HONORARY MEMBERS.

(Corrected to May 9, 1895.)

RESIDENT FELLOWS. — 195.

(Number limited to two hundred.)

CLASS I. — *Mathematical and Physical Sciences.* — 71.

SECTION I. — 17.

Mathematics and Astronomy.

Solon I. Bailey,	Arequipa, Peru.
Seth C. Chandler,	Cambridge.
Alvan G. Clark,	Cambridgeport.
J. Rayner Edmands,	Cambridge.
Benjamin A. Gould,	Cambridge.
Francis M. Green,	Boston.
Gustavus Hay,	Boston.
Henry Mitchell,	Nantucket.
Edward C. Pickering,	Cambridge.
John Ritchie, Jr.,	Boston.
John D. Runklē,	Brookline.
T. H. Safford,	Williamstown.
Edwin F. Sawyer,	Brighton.
Arthur Searle,	Cambridge.
William E. Story,	Worcester.
Henry Taber,	Worcester.
O. C. Wendell,	Cambridge.

SECTION II. — 20.

Physics.

A. Graham Bell,	Washington.
Clarence J. Blake,	Boston.
Francis Blake,	Weston.
John H. Blake,	Boston.
Charles R. Cross,	Boston.
Amos E. Dolbear,	Somerville.
Edwin H. Hall,	Cambridge.
Silas W. Holman,	Boston.
William L. Hooper,	Somerville.
William W. Jacques,	Newton.
Alonzo S. Kimball,	Worcester.
T. C. Mendenhall,	Worcester.
Benjamin O. Peirce,	Cambridge.
Edward S. Ritchie,	Newton.
A. Lawrence Rotch,	Boston.
Wallace C. Sabine,	Cambridge.
Elihu Thomson,	Lynn.
John Trowbridge,	Cambridge.
A. G. Webster,	Worcester.
Harold Whiting,	Berkeley, Cal.

SECTION III. — 21.

Chemistry.

Samuel Cabot,	Boston.
Arthur M. Comey,	Cambridge.
Thos. M. Drown,	Lehigh, Pa.
Charles W. Eliot,	Cambridge.
Thomas Gaffield,	Boston.
Henry B. Hill,	Cambridge.

Henry M. Howe,	Boston.
Charles L. Jackson,	Cambridge.
Leonard P. Kinnicutt,	Worcester.
Charles F. Mabery,	Cleveland, O.
Arthur Michael,	Somerville.
George D. Moore,	Worcester.
Charles E. Munroe,	Washington.
John U. Nef,	Chicago.
Robert H. Richards,	Boston.
Theodore W. Richards,	Cambridge.
Charles R. Sanger,	St. Louis.
Stephen P. Sharples,	Cambridge.
Francis H. Storer,	Boston.
Charles H. Wing,	Ledger, N. C.
Edward S. Wood,	Boston.

Section IV. — 13.

Technology and Engineering.

Eliot C. Clarke,	Boston.
Gaetano Lanza,	Boston.
E. D. Leavitt,	Cambridgeport.
William R. Livermore,	Boston.
Hiram F. Mills,	Lowell.
Cecil H. Peabody,	Boston.
Alfred P. Rockwell,	Boston.
Andrew H. Russell,	Rock Island, Ill.
Peter Schwamb,	Arlington.
Charles S. Storrow,	Boston.
George F. Swain,	Boston.
William Watson,	Boston.
Morrill Wyman,	Cambridge.

Class II. — *Natural and Physiological Sciences.* — 63.

Section I. — 13.

Geology, Mineralogy, and Physics of the Globe.

Thomas T. Bouvé,	Boston.
H. H. Clayton,	Milton.
Algernon Coolidge,	Boston.
William O. Crosby,	Boston.
William M. Davis,	Cambridge.
O. W. Huntington,	Cambridge.
Robert T. Jackson,	Boston.
Jules Marcou.	Cambridge.
William H. Niles,	Cambridge.
John E. Pillsbury.	Boston.
Nathaniel S. Shaler,	Cambridge.
Warren Upham,	Cleveland, O.
John E. Wolff,	Cambridge.

Section II. — 9.

Botany.

William G. Farlow,	Cambridge.
Charles E. Faxon,	Boston.
George L. Goodale,	Cambridge.
H. H. Hunnewell,	Wellesley.
B. L. Robinson,	Cambridge.
Charles S. Sargent,	Brookline.
Arthur B. Seymour,	Cambridge.
Charles J. Sprague,	Boston.
Roland Thaxter,	Cambridge.

Section III. — 24.

Zoölogy and Physiology.

Alexander Agassiz,	Cambridge.
Robert Amory,	Boston.
James M. Barnard,	Milton.
Henry P. Bowditch,	Boston.
William Brewster,	Cambridge.
Louis Cabot,	Brookline.
W. T. Councilman,	Boston.
Charles B. Davenport,	Cambridge.
Harold C. Ernst,	Boston.
J. Walter Fewkes,	Boston.
Edward G. Gardiner,	Boston.
Samuel Henshaw,	Cambridge.
Alpheus Hyatt,	Cambridge.
John S. Kingsley,	Somerville.
Theodore Lyman,	Brookline.
Edward L. Mark,	Cambridge.
Charles S. Minot,	Boston.
Edward S. Morse,	Salem.
George H. Parker,	Cambridge.
James J. Putnam.	Boston.
Samuel H. Scudder,	Cambridge.
William T. Sedgwick,	Boston.
James C. White,	Boston.
William M. Woodworth,	Cambridge.

SECTION IV. — 17.

Medicine and Surgery.

Samuel L. Abbot,	Boston.
Edward H. Bradford,	Boston.
Arthur T. Cabot,	Boston.
David W. Cheever,	Boston.
Benjamin E. Cotting,	Roxbury.
Frank W. Draper,	Boston.
Thomas Dwight,	Boston.
Reginald H. Fitz,	Boston.
Charles F. Folsom,	Boston.
Richard M. Hodges,	Boston.
Frederick I. Knight,	Boston.
Francis Minot,	Boston.
Samuel J. Mixter,	Boston.
W. L. Richardson,	Boston.
Henry P. Walcott,	Cambridge.
John C. Warren,	Boston.
Henry W. Williams,	Boston.

CLASS III. — *Moral and Political Sciences.* — 61.

SECTION I. — 10.

Philosophy and Jurisprudence.

James B. Ames,	Cambridge.
Charles C. Everett,	Cambridge.
Horace Gray,	Boston.
John C. Gray,	Boston.
G. Stanley Hall,	Worcester.
Nathaniel Holmes,	Cambridge.
John E. Hudson,	Boston.
John Lowell,	Newton.
Josiah Royce,	Cambridge.
James B. Thayer,	Cambridge.

SECTION II. — 20.

Philology and Archæology.

William S. Appleton,	Boston.
Charles P. Bowditch,	Boston.
Lucien Carr,	Cambridge.
Franklin Carter,	Williamstown.
Joseph T. Clarke,	Boston.
Henry G. Denny,	Boston.
Epes S. Dixwell,	Cambridge.
William Everett,	Quincy.
William W. Goodwin,	Cambridge.
Henry W. Haynes,	Boston.
Bennett H. Nash,	Boston.
Frederick W. Putnam,	Cambridge.
Edward Robinson,	Boston.
F. B. Stephenson,	Boston.
Joseph H. Thayer,	Cambridge.
Crawford H. Toy,	Cambridge.
John W. White,	Cambridge.
Justin Winsor,	Cambridge.
John H. Wright,	Cambridge.
Edward J. Young,	Waltham.

SECTION III. — 18.

Political Economy and History.

Charles F. Adams,	Lincoln.
Edward Atkinson,	Boston.
Edmund H. Bennett,	Boston.
Mellen Chamberlain,	Chelsea.
John Cummings,	Woburn.
Andrew M. Davis,	Cambridge.
Charles F. Dunbar,	Cambridge.
Samuel Eliot,	Boston.
John Fiske,	Cambridge.
A. C. Goodell, Jr.,	Salem.
Henry C. Lodge,	Nahant.
Augustus Lowell,	Boston.
Silas M. Macvane,	Cambridge.
John C. Ropes,	Boston.
Denman W. Ross,	Cambridge.
Charles C. Smith,	Boston.
F. W. Taussig,	Cambridge.
Francis A. Walker,	Boston.

Section IV. — 13.

Literature and the Fine Arts.

Francis Bartlett,	Boston.
John Bartlett,	Cambridge.
George S. Boutwell,	Groton.
Martin Brimmer,	Boston.
J. Elliot Cabot,	Brookline.
Francis J. Child,	Cambridge.
T. W. Higginson,	Cambridge.
S. R. Koehler,	Boston.
Charles G. Loring,	Boston.
Percival Lowell,	Brookline.
Charles Eliot Norton,	Cambridge.
Horace E. Scudder,	Cambridge.
Barrett Wendell,	Boston.

ASSOCIATE FELLOWS. — 95.

(Number limited to one hundred. Elected as vacancies occur.)

CLASS I. — *Mathematical and Physical Sciences.* — 36.

SECTION I. — 15.

Mathematics and Astronomy.

Edward E. Barnard,	San José, Cal.
S. W. Burnham,	Chicago.
George Davidson,	San Francisco.
Fabian Franklin,	Baltimore.
Asaph Hall,	Washington.
George W. Hill,	Washington.
E. S. Holden,	San José, Cal.
James E. Keeler,	Allegany, Pa.
Emory McClintock,	New York.
Simon Newcomb,	Washington.
H. A. Newton,	New Haven.
William A. Rogers,	Waterville, Me.
George M. Searle,	Washington.
J. N. Stockwell,	Cleveland, O.
Chas. A. Young,	Princeton, N.J.

SECTION II. — 7.

Physics.

Carl Barus,	Washington.
J. Willard Gibbs,	New Haven.
S. P. Langley,	Washington.
A. M. Mayer,	Hoboken, N. J.
A. A. Michelson,	Chicago.
Ogden N. Rood,	New York.
H. A. Rowland,	Baltimore.

SECTION III. — 8.

Chemistry.

Wolcott Gibbs,	Newport.
Frank A. Gooch,	New Haven.
S. W. Johnson,	New Haven.
M. Carey Lea,	Philadelphia.
J. W. Mallet,	Charlottesville, Va.
E. W. Morley,	Cleveland, O.
J. M. Ordway,	New Orleans.
Ira Remsen,	Baltimore.

SECTION IV. — 6.

Technology and Engineering.

Henry L. Abbot,	New York.
Cyrus B. Comstock,	Washington.
W. P. Craighill,	Washington.
F. R. Hutton,	New York.
George S. Morison,	Chicago.
William Sellers,	Philadelphia.

CLASS II. — *Natural and Physiological Sciences.* — 32.

SECTION I. — 15.

Geology, Mineralogy, and Physics of the Globe.

Cleveland Abbe,	Washington.
George J. Brush,	New Haven.
Edward S. Dana,	New Haven.
Walter G. Davis,	Cordova, Arg.
Sir J. W. Dawson,	Montreal.
G. K. Gilbert,	Washington.
James Hall,	Albany, N.Y.
Clarence King,	New York.
Joseph LeConte,	Berkeley, Cal.
J. Peter Lesley,	Philadelphia.
J. W. Powell,	Washington.
S. L. Penfield,	New Haven.
R. Pumpelly,	Newport, R.I.
A. R. C. Selwyn,	Ottawa.
G. C. Swallow,	Columbia, Mo.

Section II. — 4.

Botany.

A. W. Chapman,	Apalachicola, Fla.
D. C. Eaton,	New Haven.
W. Trelease,	St. Louis.
John D. Smith,	Baltimore.

Section III. — 8.

Zoölogy and Physiology.

Joel A. Allen,	New York.
W. K. Brooks,	Baltimore.
George B. Goode,	Washington.
O. C. Marsh,	New Haven.
H. N. Martin,	Baltimore.
S. Weir Mitchell,	Philadelphia.
A. S. Packard,	Providence.
A. E. Verrill,	New Haven.

Section IV. — 5.

Medicine and Surgery.

John S. Billings,	Washington.
Jacob M. Da Costa,	Philadelphia.
W. A. Hammond,	New York.
Alfred Stillé,	Philadelphia.
H. C. Wood,	Philadelphia.

Class III. — *Moral and Political Sciences.* — 27.

Section I. — 6.

Philosophy and Jurisprudence.

T. M. Cooley,	Ann Arbor, Mich.
D. R. Goodwin,	Philadelphia.
A. G. Haygood,	Oxford, Ga.
Charles S. Peirce,	New York.
T. R. Pynchon,	Hartford, Conn.
Jeremiah Smith,	Cambridge.

Section II. — 6.

Philology and Archæology.

A. N. Arnold,	Pawtuxet, R.I.
Timothy Dwight,	New Haven.
D. C. Gilman,	Baltimore.
A. C. Kendrick,	Rochester, N.Y.
E. E. Salisbury,	New Haven.
A. D. White,	Ithaca, N.Y.

Section III. — 9.

Political Economy and History.

Henry Adams,	Washington.
G. P. Fisher,	New Haven.
M. F. Force,	Cincinnati.
H. E. Von Holst,	Chicago.
Henry C. Lea,	Philadelphia.
Edward J. Phelps,	Burlington, Vt.
W. G. Sumner,	New Haven.
J. H. Trumbull,	Hartford, Conn.
David A. Wells,	Norwich, Conn.

Section IV. — 6.

Literature and the Fine Arts.

James B. Angell,	Ann Arbor, Mich.
L. P. di Cesnola,	New York.
F. E. Church,	New York.
R. S. Greenough,	Florence.
William W. Story,	Rome.
W. R. Ware,	New York.

FOREIGN HONORARY MEMBERS.—67.

(Number limited to seventy-five. Elected as vacancies occur.)

CLASS I.—*Mathematical and Physical Sciences.*—23.

SECTION I.—10.

Mathematics and Astronomy.

Arthur Auwers,	Berlin.
Francesco Brioschi,	Milan.
J. H. W. Döllen,	Dorpat.
H. A. E. A. Faye,	Paris.
Hugo Gyldén,	Stockholm.
Charles Hermite,	Paris.
William Huggins,	London.
Otto Struve,	Pulkowa.
J. J. Sylvester,	Oxford.
H. C. Vogel,	Potsdam.

SECTION II.—2.

Physics.

Lord Rayleigh,	Witham.
Sir G. G. Stokes,	Cambridge.

SECTION III.—8.

Chemistry.

Adolf Baeyer,	Munich.
Marcellin Berthelot,	Paris.
Robert Bunsen,	Heidelberg.
August Kekulé,	Bonn.
Mendeleeff,	St. Petersburg.
Victor Meyer,	Heidelberg.
Sir H. E. Roscoe,	London.
Julius Thomsen,	Copenhagen.

SECTION IV.—3.

Technology and Engineering.

Sir Henry Bessemer,	London.
Lord Kelvin,	Glasgow.
Maurice Lévy,	Paris.

CLASS II.—*Natural and Physiological Sciences.*—25.

SECTION I.—6.

Geology, Mineralogy, and Physics of the Globe.

H. Ernst Beyrich,	Berlin.
Alfred Des Cloizeaux,	Paris.
A. E. Nordenskiöld,	Stockholm.
C. F. Rammelsberg,	Berlin.
Henry C. Sorby,	Sheffield.
Heinrich Wild,	St. Petersburg.

SECTION II.—6.

Botany.

J. G. Agardh,	Lund.
E. Bornet,	Paris.
Sir Joseph D. Hooker,	London.
Baron von Mueller,	Melbourne.
Julius Sachs,	Würzburg.
Eduard Strasburger,	Bonn.

SECTION III. — 10.

Zoölogy and Physiology.

Du Bois-Reymond,	Berlin.
Ludimar Hermann,	Königsberg.
Thomas H. Huxley,	London.
Albrecht Kölliker,	Würzburg.
Lacaze-Duthiers,	Paris.
Rudolph Leuckart,	Leipsic.
Sven Lovén,	Stockholm.
C. F. W. Ludwig,	Leipsic.
Louis Pasteur,	Paris.
J. J. S. Steenstrup,	Copenhagen.

SECTION IV. — 3.

Medicine and Surgery.

Sir Joseph Lister,	London.
Sir James Paget,	London.
Rudolph Virchow,	Berlin.

CLASS III. — *Moral and Political Sciences.* — 19.

SECTION I. — 3.

Philosophy and Jurisprudence.

James Martineau,	London.
Henry Sidgwick,	Cambridge.
Sir Frederick Pollock,	Oxford.

SECTION II. — 6.

Philology and Archæology.

Ingram Bywater,	Oxford.
Sir John Evans,	Hemel Hempstead.
Pascual de Gayangos,	Madrid.
J. W. A. Kirchhoff,	Berlin.
G. C. C. Maspero,	Paris.
Max Müller,	Oxford.

SECTION III. — 7.

Political Economy and History.

Duc de Broglie,	Paris.
James Bryce,	Oxford.
Ernst Curtius,	Berlin.
W. E. Gladstone,	Hawarden.
Theodor Mommsen,	Berlin.
Jules Simon,	Paris.
William Stubbs,	Oxford.

SECTION IV. — 3.

Literature and the Fine Arts.

Jean Léon Gérôme,	Paris.
John Ruskin,	Coniston.
Leslie Stephen,	London.

STATUTES AND STANDING VOTES.

STATUTES.

(*Adopted May* 30, 1854: *amended September* 8, 1857, *November* 12, 1862, *May* 24, 1864, *November* 9, 1870, *May* 27, 1873, *January* 26, 1876, *June* 16, 1886, *October* 8, 1890, *January* 11 *and May* 10, 1893, *April* 11, *May* 9, *and October* 10, 1894, *and March* 13, *April* 10, *and May* 8, 1895.

CHAPTER I.

OF FELLOWS AND FOREIGN HONORARY MEMBERS.

1. The Academy consists of *Fellows* and *Foreign Honorary Members.* They are arranged in three Classes, according to the Arts and Sciences in which they are severally proficient, viz.: Class I. The Mathematical and Physical Sciences; — Class II. The Natural and Physiological Sciences; — Class III. The Moral and Political Sciences. Each Class is divided into four Sections, viz.: Class I., Section 1. Mathematics and Astronomy; — Section 2. Physics; — Section 3. Chemistry; — Section 4. Technology and Engineering. Class II., Section 1. Geology, Mineralogy, and Physics of the Globe; — Section 2. Botany; — Section 3. Zoölogy and Physiology; — Section 4. Medicine and Surgery. Class III., Section 1. Philosophy and Jurisprudence; — Section 2. Philology and Archæology; — Section 3. Political Economy and History; — Section 4. Literature and the Fine Arts.

2. Fellows, resident in the State of Massachusetts, only, may vote at the meetings of the Academy.* Each Resident Fellow shall pay an admission fee of ten dollars and such annual assessment, not exceeding ten dollars, as shall be voted by the Academy at each Annual Meeting.

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* The number of Resident Fellows is limited by the Charter to 200.

3. Fellows residing out of the State of Massachusetts shall be known and distinguished as Associate Fellows. They shall not be liable to the payment of any fees or annual dues, but on removing within the State shall be admitted to the privileges,* and be subject to the obligations, of Resident Fellows. The number of Associate Fellows shall not exceed *one hundred*, of whom there shall not be more than *forty* in either of the three Classes of the Academy.

4. The number of Foreign Honorary Members shall not exceed *seventy-five;* and they shall be chosen from among persons most eminent in foreign countries for their discoveries and attainments in either of the three departments of knowledge above enumerated. And there shall not be more than *thirty* Foreign Members in either of these departments.

CHAPTER II.

Of Officers.

1. There shall be a President, three Vice-Presidents, one for each Class, a Corresponding Secretary, a Recording Secretary, a Treasurer, and a Librarian, which officers shall be annually elected, by ballot, at the Annual Meeting, on the second Wednesday in May.

2. At the same time, and in the same manner, nine Councillors shall be elected, three from each Class of the Academy, but the same Fellows shall not be eligible on more than three successive years. These nine Councillors, with the President, the three Vice-Presidents, the two Secretaries, the Treasurer, and the Librarian, shall constitute the Council. It shall be the duty of this Council to exercise a discreet supervision over all nominations and elections. With the consent of the Fellow interested, they shall have power to make transfers between the several Sections of the same Class, reporting their action to the Academy.

3. If any office shall become vacant during the year, the vacancy shall be filled by a new election, and at the next stated meeting, or at a meeting called for this purpose.

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* Associate Fellows may attend, but cannot vote, at meetings of the Academy. See Chapter I. 2.

CHAPTER III.

OF NOMINATIONS OF OFFICERS.

1. At the stated meeting in March, the President shall appoint from the next retiring Councillors a Nominating Committee of three Fellows, one for each class.

2. It shall be the duty of this Nominating Committee to prepare a list of candidates for the offices of President, Vice-Presidents, Corresponding Secretary, Recording Secretary, Treasurer, Librarian, Councillors, and the Standing Committees which are chosen by ballot; and to cause this list to be sent by mail to all the Resident Fellows of the Academy not later than four weeks before the Annual Meeting.

3. Independent nominations for any office, signed by at least five Resident Fellows and received by the Recording Secretary not less than ten days before the Annual Meeting, shall be inserted in the call for the Annual Meeting, which shall then be issued not later than one week before that meeting.

4. The Recording Secretary shall prepare for use, in voting at the Annual Meeting, a ballot containing the names of all persons nominated for office under the conditions given above.

5. When an office is to be filled at any other time than at the Annual Meeting, the President shall appoint a Nominating Committee, in accordance with the provisions of Section 1, which shall announce its nomination in the manner prescribed in Section 2 at least two weeks before the time of election. Independent nominations, signed by at least five Resident Fellows and received by the Recording Secretary not later than one week before the meeting for election, shall be inserted in the call for that meeting.

CHAPTER IV.

OF THE PRESIDENT.

1. It shall be the duty of the President, and, in his absence, of the senior Vice-President present, or next officer in order as above enumerated, to preside at the meetings of the Academy; to summon extraordinary meetings, upon any urgent occasion; and to execute or see to the execution of the Statutes of the

Academy. Length of continuous membership in the Academy shall determine the seniority of the Vice-Presidents.

2. The President, or, in his absence, the next officer as above enumerated, is empowered to draw upon the Treasurer for such sums of money as the Academy shall direct. Bills presented on account of the Library, or the Publications of the Academy, must be previously approved by the respective committees on these departments.

3. The President, or, in his absence, the next officer as above enumerated, shall nominate members to serve on the different committees of the Academy which are not chosen by ballot.

4. Any deed or writing to which the common seal is to be affixed shall be signed and sealed by the President, when thereto authorized by the Academy.

CHAPTER V.

Of Standing Committees.

1. At the Annual Meeting there shall be chosen the following Standing Committees, to serve for the year ensuing, viz.: —

2. The Committee of Finance, to consist of the President, Treasurer, and one Fellow chosen by ballot, who shall have charge of the investment and management of the funds and trusts of the Academy. The general appropriations for the expenditures of the Academy shall be moved by this Committee at the Annual Meeting, and all special appropriations from the general and publication funds shall be referred to or proposed by this Committee.

3. The Rumford Committee, of seven Fellows, to be chosen by ballot, who shall consider and report on all applications and claims for the Rumford Premium, also on all appropriations from the income of the Rumford Fund, and generally see to the due and proper execution of this trust.

4. The C. M. Warren Committee, of seven Fellows, to be chosen by ballot, who shall consider and report on all applications for appropriations from the income of the C. M. Warren Fund, and generally see to the due and proper execution of this trust.

5. The Committee of Publication, of three Fellows, to whom all memoirs submitted to the Academy shall be referred, and to

whom the printing of memoirs accepted for publication shall be intrusted.

6. The Committee on the Library, of three Fellows, who shall examine the Library, and make an annual report on its condition and management.

7. An Auditing Committee, of two Fellows, for auditing the accounts of the Treasurer.

CHAPTER VI.

OF THE SECRETARIES.

1. The Corresponding Secretary shall conduct the correspondence of the Academy, recording or making an entry of all letters written in its name, and preserving on file all letters which are received; and at each meeting he shall present the letters which have been addressed to the Academy since the last meeting. With the advice and consent of the President, he may effect exchanges with other scientific associations, and also distribute copies of the publications of the Academy among the Associate Fellows and Foreign Honorary Members, as shall be deemed expedient; making a report of his proceedings at the Annual Meeting. Under the direction of the Council for Nomination, he shall keep a list of the Fellows, Associate Fellows, and Foreign Honorary Members, arranged in their Classes and in Sections in respect to the special sciences in which they are severally proficient; and he shall act as secretary to the Council.

2. The Recording Secretary shall have charge of the Charter and Statute-book, journals, and all literary papers belonging to the Academy. He shall record the proceedings of the Academy at its meetings; and after each meeting is duly opened, he shall read the record of the preceding meeting. He shall notify the meetings of the Academy, and apprise committees of their appointment. He shall post up in the Hall a list of the persons nominated for election into the Academy; and when any individual is chosen, he shall insert in the record the names of the Fellows by whom he was nominated.

3. The two Secretaries, with the Chairman of the Committee of Publication, shall have authority to publish such of the proceedings of the Academy as as may seem to them calculated to promote the interests of science.

CHAPTER VII.

OF THE TREASURER.

1. The Treasurer shall give such security for the trust reposed in him as the Academy shall require.

2. He shall receive officially all moneys due or payable, and all bequests or donations made to the Academy, and by order of the President or presiding officer shall pay such sums as the Academy may direct. He shall keep an account of all receipts and expenditures; shall submit his accounts to the Auditing Committee; and shall report the same at the expiration of his term of office.

3. The Treasurer shall keep a separate account of the income and appropriation of the Rumford Fund, and report the same annually.

4. All moneys which there shall not be present occasion to expend shall be invested by the Treasurer, under the direction of the Finance Committee, on such securities as the Academy shall direct.

CHAPTER VIII.

OF THE LIBRARIAN AND LIBRARY.

1. It shall be the duty of the Librarian to take charge of the books, to keep a correct catalogue of same, and to provide for the delivery of books from the Library. He shall also have the custody of the publications of the Academy.

2. The Librarian, in conjunction with the Committee on the Library, shall have authority to expend, as they may deem expedient, such sums as may be appropriated, either from the Rumford or the General Fund of the Academy, for the purchase of books, and for defraying other necessary expenses connected with the Library. They shall have authority to propose rules and regulations concerning the circulation, return, and safe-keeping of books; and to appoint such agents for these purposes as they may think necessary.

3. To all books in the Library procured from the income of the Rumford Fund, the Librarian shall cause a stamp or label to be affixed, expressing the fact that they were so procured.

4. Every person who takes a book from the Library shall give a receipt for the same to the Librarian or his assistant.

5. Every book shall be returned in good order, regard being had to the necessary wear of the book with good usage. And if any book shall be lost or injured, the person to whom it stands charged shall replace it by a new volume or set, if it belongs to a set, or pay the current price of the volume or set to the Librarian; and thereupon the remainder of the set, if the volume belonged to a set, shall be delivered to the person so paying for the same.

6. All books shall be returned to the Library for examination at least one week before the Annual Meeting.

CHAPTER IX.

Of Meetings.

1. There shall be annually four stated meetings of the Academy; namely, on the second Wednesday in May (the Annual Meeting), on the second Wednesday in October, on the second Wednesday in January, and on the second Wednesday in March. At these meetings only, or at meetings adjourned from these and regularly notified, shall appropriations of money be made, or alterations of the statutes or standing votes of the Academy be effected.

2. Fifteen Fellows shall constitute a quorum for the transaction of business at a stated meeting. Seven Fellows shall be sufficient to constitute a meeting for scientific communications and discussions.

3. The Recording Secretary shall notify the meetings of the Academy to each Fellow residing in Boston and the vicinity; and he may cause the meetings to be advertised, whenever he deems such further notice to be needful.

CHAPTER X.

OF THE ELECTION OF FELLOWS AND HONORARY MEMBERS.

1. Elections shall be made by ballot, and only at stated meetings.

2. Candidates for election as Resident Fellows must be proposed by two or more Resident Fellows, in a recommendation signed by them, specifying the Section to which the nomination is made, which recommendation shall be transmitted to the Corresponding Secretary, and by him referred to the Council for Nomination. No person recommended shall be reported by the Council as a candidate for election, unless he shall have received a written approval, signed at a meeting of the Council by at least seven of its members. All nominations thus approved shall be read to the Academy at a stated meeting, and shall then stand on the nomination list during the interval between two stated meetings, and until the balloting. No person shall be elected a Resident Fellow, unless he shall have been resident in this Commonwealth one year next preceding his election. If any person elected a Resident Fellow shall neglect for one year to pay his admission fee, his election shall be void; and if any Resident Fellow shall neglect to pay his annual assessments for two years, provided that his attention shall have been called to this article, he shall be deemed to have abandoned his Fellowship; but it shall be in the power of the Treasurer, with the consent of the Council, to dispense (*sub silentio*) with the payment both of the admission fee and of the assessments, whenever in any special instance he shall think it advisable so to do.

3. The nomination of Associate Fellows shall take place in the manner prescribed in reference to Resident Fellows; and after such nomination shall have been publicly read at a stated meeting previous to that when the balloting takes place, it shall be referred to the Council for Nomination; and a written approval, authorized and signed at a meeting of said Council by at least seven of its members, shall be requisite to entitle the candidate to be balloted for. The Council may in like manner originate nominations of Associate Fellows, which must be read at a stated meeting previous to the election, and be exposed on the nomination list during the interval.

4. Foreign Honorary Members shall be chosen only after a nomination made at a meeting of the Council, signed at the time by at least seven of its members, and read at a stated meeting previous to that on which the balloting takes place.

5. Three fourths of the ballots cast must be affirmative, and the number of affirmative ballots must amount to eleven to effect an election of Fellows or Foreign Honorary Members.

6. Each Section of the Academy is empowered to present lists of persons deemed best qualified to fill vacancies occurring in the number of Foreign Honorary Members or Associate Fellows allotted to it; and such lists, after being read at a stated meeting, shall be referred to the Council for Nomination.

7. If, in the opinion of a majority of the entire Council, any Fellow — Resident or Associate — shall have rendered himself unworthy of a place in the Academy, the Council shall recommend to the Academy the termination of his Fellowship; and provided that a majority of two thirds of the Fellows at a stated meeting, consisting of not less than fifty Fellows, shall adopt this recommendation, his name shall be stricken off the roll of Fellows.

CHAPTER XI.

Of Amendments of the Statutes.

1. All proposed alterations of the Statutes, or additions to them, shall be referred to a committee, and, on their report at a subsequent meeting, shall require for enactment a majority of two thirds of the members present, and at least eighteen affirmative votes.

2. Standing Votes may be passed, amended, or rescinded, at any stated meeting, by a majority of two thirds of the members present. They may be suspended by a unanimous vote.

CHAPTER XII.

Of Literary Performances.

1. The Academy will not express its judgment on literary or scientific memoirs or performances submitted to it, or included in its publications.

STANDING VOTES.

1. Communications of which notice had been given to the Secretary shall take precedence of those not so notified.

2. Resident Fellows who have paid all fees and dues chargeable to them are entitled to receive one copy of each volume or article printed by the Academy, on application to the Librarian personally or by written order, within two years from the date of publication. And the current issues of the Proceedings shall be supplied, when ready for publication, free of charge, to all the Fellows and members of the Academy who desire to receive them.

3. The Committee of Publication shall fix from time to time the price at which the publications of the Academy may be sold. But members may be supplied at half this price with volumes which they are not entitled to receive free, and which are needed to complete their sets.

4. Two hundred extra copies of each paper accepted for publication in the Memoirs or Proceedings of the Academy shall be placed at the disposal of the author, free of charge.

5. Resident Fellows may borrow and have out from the Library six volumes at any one time, and may retain the same for three months, and no longer.

6. Upon special application, and for adequate reasons assigned, the Librarian may permit a larger number of volumes, not exceeding twelve, to be drawn from the Library for a limited period.

7. Works published in numbers, when unbound, shall not be taken from the Hall of the Academy, except by special leave of the Librarian.

8. Books, publications, or apparatus shall be procured from the income of the Rumford Fund only on the certificate of the Rumford Committee that they, in their opinion, will best facilitate and encourage the making of discoveries and improvements which may merit the Rumford Premium.

9. The Annual Meeting and the other stated meetings shall be holden at eight o'clock, P. M.

10. A meeting for receiving and discussing scientific communications may be held on the second Wednesday of each month not appointed for stated meetings, excepting July, August, and September.

RUMFORD PREMIUM.

In conformity with the terms of the gift of Benjamin, Count Rumford, granting a certain fund to the American Academy of Arts and Sciences, and with a decree of the Supreme Judicial Court for carrying into effect the general charitable intent and purpose of Count Rumford, as expressed in his letter of gift, the Academy is empowered to make from the income of said fund, as it now exists, at any Annual Meeting, an award of a gold and silver medal, being together of the intrinsic value of three hundred dollars, as a premium to the author of any important discovery or useful improvement in light or in heat, which shall have been made and published by printing, or in any way made known to the public, in any part of the continent of America, or any of the American islands; preference being always given to such discoveries as shall, in the opinion of the Academy, tend most to promote the good of mankind; and to add to such medals, as a further premium for such discovery and improvement, if the Academy see fit so to do, a sum of money not exceeding three hundred dollars.

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